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### III.

#### *On the Impurities of Commercial Zinc, with special Reference to the Residue insoluble in Dilute Acids, to Sulphur, and to Arsenic.*

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WHEN common zinc is dissolved in dilute acids, as in the ordinary process of preparing hydrogen, a finely divided black substance remains undissolved, sometimes floating, sometimes sinking in the liquid. The blackness and apparent lightness of this residue from zinc dissolved in dilute acids seem to indicate that it is carbon, which may perhaps account for the widely spread error that carbon is the chief admixture in crude zinc, as it is in cast-iron. This error has been often corrected, but the information on the whole subject lacks precision and certainty. The statements of the best authorities in regard to the impurities of zinc are for the most part loose, inaccurate, and sometimes contradictory.\* To obtain precise and definite knowledge, if possible, of the chief impurities of this important metal, this investigation was undertaken.

\* The black residue was observed and experimented upon by HELLOT (*Mémoires de l'Académie des Sciences*, 1735, [Mem.] p. 18, *et seq.*) and by DE LASSONE (*Ibid.* 1777, [Mem.] p. 11 *et seq.*)

BERGMANN says, in his *Physical and Chemical Essays*, translated by Cullen, London, 1788, II. 321, that pure zinc is extremely rare, and commends the zinc brought by Grill from China as containing scarcely half of one per cent of lead; the zinc of Goslar is stated to contain somewhat more lead, but neither of these zincs contained the smallest particle of iron.

FOURCROY. For an express statement that this black powder is *plumbago*, see Fourcroy's *Elements of Natural History and Chemistry*, translated from the Paris edition of 1789, London, 1790, II. 289.

PROUST. "It is commonly thought that the black powder, which separates from its (zinc's) solution in sulphuric acid, is charcoal or a carbide of zinc: it is nothing but arsenic, mixed with a little lead and copper, which the reducing power of the zinc precipitates in the metallic state." *Savans Étrangers*, [2.] I. 211 (Paris, published in 1806). "Iron is found in very large quantity in it (zinc), and sometimes manganese." *Ibid.* 212. It should be remarked, that the precipitate produced by sulphuretted hydrogen, and called arsenic

In order to make the results obtained as general as possible, we have examined authentic specimens of all the commercial zincs which we were able to procure. These are : —

by Proust, was most probably cadmium, — a metal not discovered till 1817. (See Gilbert's *Annalen der Phys.*, 1819, LX. 193.) This consideration is important, as it may serve to explain the very loose statements about arsenic in zinc which have since prevailed.

VAUQUELIN, in reporting on this memoir of Proust, says: "It has been, and still is generally thought that the black powder . . . . . consists of carbide of iron." *Annales de Chimie*, 1800, XXXV. 51.

See also a remark by PROUST, similar to that above quoted, on the impurities of zinc, in *Annales de Chimie*, 1803, LI. 72.

FOURCROY. "In proportion as this solution (in sulphuric acid) takes place, we see a small quantity of very black powder in a state of extreme division floating in the liquid, which has long been mistaken by chemists, and which is nothing else than carburet of iron or plumbago, existing originally in the zinc." *Système des Connaiss. Ch.*, V. 377. See also the English translation, London, 1804, V. 533.

VOGEL. "The black residue (from the sulphuric acid solution of commercial zinc) consists of carbon, iron, and sulphate of lead. French zinc contains neither copper nor arsenic, but a small quantity of lead." *Schweigger's Journal für Ch. u. Phys.*, 1814, XI. 418. This observer expressly contradicts the statements of Proust and Thomson [*vide infra*] in regard to copper and arsenic.

BERZELIUS and DULONG give the impurities of commercial zinc as follows: — lead, tin, copper, iron, cadmium, and sulphur. *Ann. de Ch. et Phys.*, 1820, XV. 388.

HOUTON LABILLARDIÈRE says: "I have examined several times the residue which the zinc of commerce leaves when dissolved in weak sulphuric acid; I have always found that it was formed of tin and of traces of iron; I have never encountered lead, although it is possible that some sorts of zinc contain it." *Thenard's Traité de Chimie*, Paris, 1824, V. 307.

THOMSON. "It (the zinc of commerce) is never quite free from carbon; . . . . it contains, likewise, small quantities of several metals." *First Principles of Chemistry*, 1825, I. 52.

W. HENRY. "The zinc of commerce is never pure, but contains charcoal, lead, and sulphur. . . . . Even after careful distillation, zinc is still liable to contain a small quantity of charcoal." *Elements of Experimental Chemistry*, 11th edition, 1829, II. 16.

These statements of the impurities of zinc have been extensively copied. "The common zinc of commerce generally contains a portion of lead, copper, iron, traces of arsenic and manganese, and a little plumbago: these impurities chiefly remain in the form of a black powder when it is dissolved in dilute sulphuric acid." *BRANDE'S Manual of Chemistry*, 3d edition, 1830, II. 42.

DE LA RIVE and PLANCHE. "Commercial zinc contains traces of tin, lead, and sometimes more than one per cent of iron; also, a considerable amount of cadmium." From the *Bibliothèque Universelle*, in *Pogg. Ann.*, 1830, XIX. 234. See also *Ann. de Ch. et Phys.*, XLIII. 437.

SCHLINDLER has found in commercial zinc, iron, lead, arsenic, copper, nickel, cobalt, manganese, carbon, and a small amount of uranium. *Berzelius's Jahres-Bericht*, 1832, XI. 126. This determination of uranium has been doubted by all subsequent observers.

"The following impurities in commercial zinc occur: — lead, arsenic, iron, copper, cadmium, antimony, manganese, nickel, cobalt, sulphur, and carbon." *Brandes*, in reporting on the prize essays of BONNET and others upon the oxide of zinc. *Ann. der Pharm.*, 1834, IX. 184.

1. Silesian zinc.
2. Vieille Montagne (Belgian) zinc.
3. New Jersey (American) zinc.

WACKENRODER, in an excellent paper on the oxide of zinc, maintains that the principal impurities of *Silesian* zinc are lead, cadmium, and iron. He found no arsenic in his own experiments, but admits the possibility of its occurrence in small quantities. Traces of copper he believes to exist in this zinc, but neither cobalt, nickel, nor manganese, as had been intimated by Hermann (Gilbert's *Ann. der Phys.*, LXVI. 284). He observed the development of sulphuretted hydrogen from zinc treated with dilute chlorhydric acid; but doubts the occurrence of carbon in zinc, except as minute, accidental splinters, thus contradicting Fourcroy. *Ann. der Pharm.*, 1834, X. 53.

TURNER. "It (zinc) frequently contains traces of charcoal, sulphur, cadmium, arsenic, lead, and copper; and iron is always present." *Elements of Chemistry*, 5th edition, 1834, p. 543.

FARADAY. "Most zinc leaves, when dissolved in dilute sulphuric acid, more or less residue, which contains various metals in the metallic state, as copper, lead, tin, iron, cadmium, &c." *Ann. der Pharm.*, 1836, XVII. 21.

WITTSTEIN says that the metals with which common zinc is contaminated are iron, cadmium, tin, and lead. Cited in *Ann. der Pharm.*, 1836, XX. 179.

KANE. "The zinc of commerce is impure; it contains traces of carbon, iron, cadmium, and often arsenic." *Elements of Chemistry*, 1842, p. 602.

BARRUEL says that he analyzed a quantity of the residues from zincs dissolved in dilute acid, which had accumulated in the laboratory of the Sorbonne during some years, and found in this mass (of very questionable origin) 58.5 tin, 34.5 lead, 5.5 sulphur, besides traces of iron, manganese, &c., which he did not determine. Wishing to verify this result, he examined the residue from some other zinc, and inferred that it was chiefly tin; but his own statement of the process employed would not lead to this conclusion. *Comptes Rendus*, 1842, XIV. 724.

ERDMANN and MARCHAND cite this observation in their journal, and remark in a note that an examination of similar residues gave them lead and tin, with traces of iron, carbon, and cadmium. *Journal für pr. Chem.*, 1842, XXVI. 384.

A. ERDMANN noticed the occurrence of lead in zinc, and the impossibility of completely separating the lead by redistillation, because of the partial volatilization of the lead. *Annalen der Ch. u. Pharm.*, 1844, L. 437.

BERZELIUS. "It (the zinc of commerce) contains often iron, lead, arsenic, copper, and charcoal." *Traité de Chimie*, Paris, 1846, II. 604. "We are ignorant to what extent zinc combines with carbon, but the zinc found in commerce always contains some." *Ibid.*, 616.

URE. "The ordinary zinc found in the market is never pure; but contains lead, cadmium, arsenic, copper, iron, and carbon, from some of which it may be freed in a great degree by distillation; but even after this process it retains a little lead, with all the arsenic and cadmium." *Dictionary of Arts, &c.*, 4th edition, Boston, 1853, II. 994.

PELOUZE and FREMY. "The zinc of commerce is never pure. It contains about a hundredth of its weight of foreign bodies, which are chiefly lead and iron; carbon, copper, cadmium, and arsenic are sometimes found in it." *Traité de Chimie Générale*, 2<sup>e</sup> édit., 1854, III. 35.

W. A. MILLER. "Commercial zinc contains a small quantity of lead and iron, and of a peculiar carbonaceous matter." *Elements of Chemistry*, 1856, Part II. 847.

4. Pennsylvanian zinc (Pennsylvania and Lehigh Zinc Works, Bethlehem, Penn.).
5. Vieille Montagne zinc, such as is used at the United States Mint.
6. A zinc labelled "Zinc pur," Rousseau Frères, Paris.
7. A sheet zinc of unknown origin, obtained in Berlin (Prussia).
8. An English zinc, made near Wrexham, North Wales.
9. An English zinc, from the Mines Royal, Neath, Glamorganshire.
10. An English zinc, from the works of Dillwyn and Company, Swansea.
11. An English zinc, from the works of the Messrs. Vivian, Swansea.

Our specimens of the first three spelters were obtained in blocks or ingots from the Revere Copper Company of Boston, by the kindness of John Revere, Esq.; we received our specimens of the fourth zinc in ingots, through Professor Brush of New Haven, directly from the manufacturers; the fifth zinc was procured in Philadelphia, by our friend, Professor J. P. Cooke, from the purveyors to the United States Mint. The sixth specimen was bought as pure distilled zinc, in 1856, at Paris, of MM. Rousseau Frères, dealers in pure chemicals. The four samples of English zinc are authentic specimens, for which we are indebted to the kindness of the Hon. Edward Twisleton of London. The eighth specimen is a spelter made "from silicate of zinc" at Minera, near Wrexham in North Wales; Belgian retorts are used in its manufacture, but no other details of the process are known to us.

A qualitative examination of the residues left by these zincs when treated with dilute acids, showed that they chiefly consisted of *metallic lead*. It will appear in the sequel, that lead is the chief impurity of commercial zinc, and that the carbon, tin, copper, iron, arsenic, and other impurities found in it by previous observers, occur either in very minute quantities, or rarely, and doubtless accidentally.

*Lead.* — We have determined quantitatively the amount of lead in each of the zincs above specified by the following process: — A weighed amount of each zinc was dissolved in dilute sulphuric acid, saturated with sulphate of lead. This acid was prepared by diluting common sulphuric acid with four parts of water, and allowing the mixture to settle for some days before decantation. When the zinc was dissolved, the black residue was in each case separated from the solution by decantation, treated with a few drops of nitric acid, and gently evaporated to dryness. The white residue thus obtained was then washed with the same dilute acid into the original solution of the zinc, which was filtered after standing forty-eight hours, and the precipitated sulphate of lead was weighed on a tared filter. The results of these analyses are given in the following table: —

TABLE I.

(1.) Name of Zinc.	(2.) Weight of Zinc taken.	(3.) Weight of Pb O, S O <sub>3</sub> .	(4.) Corresponding Weight of Lead.	(5.) Amount of Lead in per cent.
	grammes.	gramme.	gramme.	per cent.
Silesian . . .	23.8066	0.5082	0.3472	1.46
Vieille Montagne . . .	25.2795	0.108	0.0738	0.292
New Jersey . . .	28.672	0.033	0.0225	0.079
Pennsylvania . . .	26.522	No residue.	0.0000	0.000
Mint . . .	24.5308	0.1768	0.1212	0.494
Rousseau Frères . . .	24.3432	0.0379	0.0259	0.106
Berlin . . .	23.074	0.4381	0.299	1.297
Wrexham . . .	29.999	0.5235	0.3569	1.192
Mines Royal . . .	38.8276	0.469	0.3197	0.823
Dillwyn & Co. . .	31.6425	0.771	0.5256	1.661
Messrs. Vivian . . .	27.724	0.6165	0.4203	1.516

Two points in the process required examination. In the first place, it was undesirable to use pure sulphuric acid, because sulphate of lead is not absolutely insoluble in dilute sulphuric acid; but the question suggested itself, whether by employing acid saturated with sulphate of lead, we might not introduce lead which would subsequently be weighed as sulphate. The following experiment answered this question. 0.2198 gram. of pure lead (*Probirblei* from the laboratory of Professor Plattner in Freiberg) was dissolved in pure dilute nitric acid, the solution evaporated to dryness, the residue so obtained dissolved in hot water, and precipitated as sulphate in 250 c. c. of our dilute sulphuric acid (one part of commercial acid and four parts of water.)

Weight of pure lead taken	gramme. 0.2198
“ “ sulphate on a tared filter	0.3219
“ “ lead in 0.3219 gram. Pb O, S O <sub>3</sub>	0.2199

After weighing the sulphate on a tared filter, we ignited the filter and precipitate, and, following the method of determining sulphate of lead which is prescribed in most text-books, again weighed the sulphate after ignition.

Weight of pure lead taken	gramme. 0.2198
“ “ sulphate of lead after ignition	0.3123
“ “ lead in 0.3123 gram. Pb O, S O <sub>3</sub>	0.2134

This result conclusively proved that none of the minute quantity of lead in the sulphuric acid was weighed as sulphate at the close of the analysis. Secondly, it was necessary to inquire whether the insolubility of the sulphate of lead was diminished by the presence of a large amount of sulphate of zinc. To determine this point, a weighed amount of acetate of lead was dissolved in water, and added to a solution of

25 gram. of pure sulphate of zinc in 100 c. c. of water acidulated with 5 gram. of pure sulphuric acid. The precipitated sulphate was first weighed on a tared filter, and afterwards ignited, and again weighed. The results of two experiments are given in the following table:—

TABLE II.

	(1.) Weight of Pb O & taken.	(2.) Weight of Pb O, S O <sub>3</sub> on Tared Filter.	(3.) Weight of Pb O, S O <sub>3</sub> after Ignition.	(4.) Excess of Pb O in Col. 2 over Calculated Pb O in Col. 1.	(5.) Loss of Pb O in Col. 3, from Calculated Pb O in Col. 1.
	gramme. 1.1013 containing 0.6484 of Pb O	gramme. 0.8838 containing 0.6505 of Pb O	gramme. 0.8692 containing 0.6397 of Pb O	gramme. 0.0021	gramme. 0.0087
No. 1.					
No. 2.	1.0164 containing 0.5985 of Pb O	0.8159 containing 0.6005 of Pb O	0.8053 containing 0.5927 of Pb O	0.002	0.0058

The filtrates from the sulphate of lead precipitates in these two experiments were saturated with sulphuretted hydrogen gas during forty hours, but not a trace of lead could be detected in either case. These experiments sufficiently prove that the accuracy of the determination of lead as sulphate is not impaired by the presence of sulphate of zinc, or, at least, that, if there be any error, it is an error on the safe side, causing a loss of lead, and not a gain.\*

\* The results given in Table II., and in the immediately preceding statement of the experiment with *Probirblei*, illustrate a fact which we have had frequent occasion to observe; viz. that the sulphate of lead can be weighed more accurately on a tared filter than by any process which subjects the filter and precipitate to ignition. There is an unavoidable loss in igniting this precipitate, in consequence of the volatilization of the sulphide of lead, which is reduced from the sulphate by the paper of the filter. The common objection to weighing this precipitate on a tared filter, is the difficulty of removing the last traces of the sulphuric acid used in washing; but careful washing with alcohol will overcome this difficulty, whereas no care can prevent the loss consequent upon ignition. We ignited 1.4004 gram. of absolutely pure sulphate of lead with a fine Swedish filter 10 centimetres in diameter, cut into small pieces, moistened, and mixed with the sulphate of lead. The sulphate, after ignition, weighed 1.3826 gram.

$$\begin{array}{rcl}
 \text{Amount of lead in 1.4004 gram. Pb O SO}_3 & = & 0.95654 \\
 \text{Loss " by ignition} & = & 0.01216 \\
 \text{" " " in per cent} & = & 1.271
 \end{array}$$

In this experiment the amount of sulphate of lead used was considerable; if this amount be small, the loss by ignition will be proportionally increased. It may be objected, that it is not usual to ignite the filter with the mass of the precipitate; but, on the other hand, it is often the case that the filter ashes cannot be burnt white on the crucible cover, and moreover the process of filtration produces a very intimate contact between the paper and the fine particles of sulphate of lead which is not imitated in the above experiment.

To verify the results stated in the third column of Table I., we determined the sulphuric acid in each precipitate of sulphate of lead, by the method described by Fresenius.\* Each precipitate of sulphate of lead was digested with a solution of pure bicarbonate of soda prepared from the oxalate, and the sulphuric acid determined in the usual manner in the filtrate from the washed carbonate of lead. A comparison of columns 3 and 5 in Table III. made it at once clear that the precipitates of column 2 consisted only of sulphate of lead.

TABLE III.

(1.) Name of Zinc.	(2.) Weight of Pb O, S O <sub>3</sub> .	(3.) Sulphuric Acid in the Given Weight of Pb O, S O <sub>3</sub> .	(4.) Weight of Ba O, S O <sub>3</sub> .	(5.) Sulphuric Acid in the Found Weight of Ba O, S O <sub>3</sub> .
	gramme.	gramme.	gramme.	gramme.
Silesian . . . .	0.5082	0.1341	0.3954	0.1359
Vieille Montagne . .	0.108	0.0285	0.0845	0.029
New Jersey . . . .	0.033	0.0087	0.035	0.012
Mint . . . .	0.1768	0.0463	0.1356	0.0466
Rousseau Frères . .	0.0379	0.0100	0.0306	0.0105
Berlin . . . .	0.4381	0.1156	0.3331	0.1146
Wrexham . . . .	0.5235	0.1382	0.4282	0.1469
Mines Royal . . . .	0.469	0.1238	0.3659	0.1255
Dillwyn & Co. . . .	0.771	0.2035	0.5962	0.2045
Messrs. Vivian . . .	0.6165	0.1627	0.4780	0.1640

*Cadmium and Tin.* — The filtrates from the precipitates of sulphate of lead obtained from the zincs in Table I., except the Pennsylvania zinc, were saturated with sulphuretted hydrogen for twenty-four hours or upwards, and the small precipitates which separated were filtered off, washed quickly with sulphuretted hydrogen water, dried, and ignited; they were then treated with a few drops of nitric acid, again evaporated to dryness, ignited, and weighed. The color of these precipitates was yellowish-brown, with the single exception of the precipitate obtained from New Jersey zinc, which was blackish. When this blackish precipitate from this zinc was moistened with nitric acid, the blue-green color of the partial solution suggested the presence of copper, and a separate determination of the amount of copper in this zinc was therefore made, and will be given hereafter. The color of the precipitates from the other zincs excluded all the metals of the group precipitated by sulphuretted hydrogen, except arsenic, antimony, tin, and cadmium. The first two of these metals do not exist in zinc, as we shall hereafter show, except in exceedingly minute quantities, and even any such minute quantity would probably have been driven off by the ignition, twice repeated, of the

\* Anleitung zur Quantitativen Analyse, Braunschweig, Vierte Auflage, 1858, p. 286, § 132, II. b. β.



precipitates. The small precipitates weighed must therefore have consisted of the oxides of tin and cadmium. The results of these analyses are given in the following table. The numbers in the fourth column show what per cent each weight in column 3 is of the corresponding weight in column 2.

TABLE IV.

(1.) Name of Zinc.	(2.) Weight of Zinc taken.	(3.) Weight of the Precipitate by H <sub>2</sub> S, ignited with N O <sub>2</sub> .	(4.) In per cent of the Zinc taken, these precipitates equal.	(5.) Result of the Blowpipe test for Tin.
Silesian	grammes. 23.8066	gramme. 0.013	0.0546	No tin, or but very uncertain traces.
Vieille Montagne	25.2795	0.0071	0.0281	Distinct spangles, probably tin.
New Jersey	28.672	0.1285	0.4471	{ Abundant spangles of tin, which gave the reaction with Au <sub>2</sub> Cl <sub>3</sub> .
Mint	24.5308	0.0024	0.0098	No tin.
Rousseau Frères	24.3432	0.0099	0.0406	Faint traces of tin.
Berlin	23.074	0.0041	0.0178	Distinct spangles, probably tin.
Wrexham	29.999	0.0021	0.0070	No tin.
Mines Royal	38.8276	0.0016	0.0041	A very uncertain trace of tin.
Dillwyn & Co.	31.6425	0.0011	0.0035	Faint traces of tin.
Messrs. Vivian	27.724	0.0079	0.0285	{ Distinct spangles of tin, which gave the reaction with Au <sub>2</sub> Cl <sub>3</sub> .

If it be remembered that the weights given in the third column are not the weights of the metals themselves, but of their oxides, it will be apparent that tin and cadmium together form but a very insignificant impurity in commercial zinc. In none of the ten samples analyzed, except the New Jersey zinc, can the sum of the tin and cadmium amount to one twenty-fifth of one per cent. The precipitates whose weights are given in column 3 (except New Jersey, which alone gave indications of copper), having been moistened with nitric acid, were digested with distilled water, and then filtered. Through the filtrates sulphuretted hydrogen was passed, producing in each case a dirty-yellow cloudiness, which was too small in amount to be further examined. That portion of each precipitate which was insoluble in water, and therefore remained on the filter, was examined before the blowpipe by incinerating the filter and precipitate on charcoal, and fusing them with neutral oxalate of potassa in the reducing flame. The fused mass was ground up in an agate mortar, and examined for metallic spangles; when these were sufficient in amount, they were dissolved in chlorhydric acid, and the solution tested with terchloride of gold. The result for each zinc is stated in the fifth column of Table IV. For Silesian zinc, the Wrexham (English) zinc, and the zinc

used at the United States Mint, the results were negative. To confirm these results, 25 gram. of Silesian zinc and 20 gram. of Mint zinc were separately dissolved in dilute chlorhydric acid, and the residues separated from the solutions just before the zinc had completely disappeared, in order to collect in the residues all the tin which the zincs might contain. Each residue was then treated with strong chlorhydric acid; the chloride of lead formed was separated by decantation, and the solution tested with terchloride of gold. No trace of tin could be detected in either case.

The precipitate produced in the solution of New Jersey zinc by sulphuretted hydrogen weighed after ignition 0.1285 gram. (see Table IV.), and gave evidence of containing copper. To determine whether it also contained tin, the precipitate was treated with nitric acid, and the matter insoluble in nitric acid was collected, and found to weigh 0.0389 gram. When this insoluble residue was reduced on charcoal before the blow-pipe, it yielded metallic globules, the acid solution of which gave the characteristic reaction for tin with terchloride of gold.

*Copper.* — No spelter except that from New Jersey gave the slightest evidence of the presence of copper. We determined the per cent of copper with which that zinc was contaminated by the following method: 17.9452 gram. of the zinc were dissolved in pure chlorhydric acid, and the residue, having been treated with nitric acid, was added to the original solution, through which sulphuretted hydrogen was then passed. The precipitated sulphide of copper was filtered off, washed with sulphuretted hydrogen water, dried, and separated from the filter. The filter was then burned, and its ashes, wet with sulphide of ammonium, were added to the previously separated sulphide of copper; the whole was then ignited in a current of hydrogen, and the resulting disulphide of copper weighed.

Weight of zinc taken	. . .	17.9452 grammes.
“ “ disulphide of copper	. . .	0.0292 “
“ “ copper corresponding	. . .	0.0233 “
Per cent of copper	. . .	0.1298

In what way copper was introduced into this zinc, we do not undertake to explain.

We subsequently examined, in connection with our experiments on carbon in the residue from zinc dissolved in dilute acids, the precipitates produced by sulphuretted hydrogen in the chlorhydric-acid solutions of several different spelters. The experiments simply served to corroborate the results which have been already stated, as obtained with sulphuric-acid solutions of the different zincs, only one new fact being developed, the presence of a trace of cadmium in the Pennsylvanian zinc. From

previous experiments made by Prof. Brush we had learned that some specimens of this spelter contain noticeable quantities of Cadmium.

*Iron*—is usually to be found in commercial zinc, and enough quantitative determinations of the amount of this impurity have been already published to show that it very rarely exceeds in amount two tenths of one per cent, and that, moreover, it is an impurity introduced into the zinc from the iron moulds in which the spelter is generally cast. Karsten, in his admirable memoir on the “Admixtures which diminish the Tenacity of Zinc,” has sufficiently proved that the zinc takes up iron from the moulds, by determining the iron in the zinc before and after the process of casting. It is true that Karsten experimented upon Silesian zinc alone, but the same contamination of the spelter would be produced in any works in which the process of casting in iron moulds was used.\* We have made determinations of the iron in three samples of zinc volumetrically by permanganate of potassa,† but have thought it not worth while to multiply analyses upon a point already sufficiently clear.

1.	New Jersey zinc	gave	0.2088	per cent of iron.
2.	“ “ “	“	0.2087	“ “
3.	Mint zinc	“	0.0585	“ “
4.	“ “ “	“	0.0566	“ “
5.	Berlin zinc (sheet)	“	0.0674	“ “
6.	“ “ “ “	“	0.0549	“ “

Besides the metallic impurities which have already been mentioned, it has been stated by previous observers, in places already cited, that nickel, cobalt, manganese, arsenic, and antimony are sometimes to be found in the zinc of commerce. The pres-

\* Karsten determined the iron in three samples of “Werkzink,” by which term he designates the zinc which is the immediate product of the distillation,—a mass of drops partially fused together; and again determined the iron in the same samples after they had been cast into cakes, and converted into the crude zinc (Rohzink) as it is found in commerce. His results may be tabulated as follows:—

No.	Iron in the Werkzink.	Iron in the Rohzink.
No. 1, . . . .	0.03 per cent.	0.154 per cent.
“ 2, . . . .	0.04. “ “	0.180 “ “
“ 3, . . . .	0.05 “ “	0.210 “ “

Karsten also shows that the refined zinc, obtained by remelting the crude zinc on the hearth of a reverberatory furnace, is almost absolutely free from iron. Archiv. f. Mineralogie, Karsten u. Dechen., 1842, XVI. 623. Also, Dingler's Polyt. Jour., 1842, LXXXVI. 193.

† For the description of the method, see Mohr's Lehrbuch der Titrimethode, Zweite Abtheilung, p. 234. A sample of zinc from Stolberg gave Mohr 0.0442 per cent of iron, and a sample from Linz, on the Rhine, contained 0.126 per cent of iron.

ence of very small quantities of arsenic, and possibly of antimony, in many of the zincs of commerce is undeniable, but the amount of these metals present is so infinitesimal, that they can only be detected qualitatively by the most delicate tests, and a quantitative determination of either of them we regard as so nearly impossible as to be untrustworthy and incredible. A full discussion of the subject of arsenic as an impurity in commercial zinc will be found below. The occurrence of nickel, cobalt, and manganese in zinc has been denied just as often as it has been asserted, but it is of course impossible to assert the universal negative, that these metals are never to be found in any spelter, for zinc is an article of commerce which is manufactured in many different places, by various processes, from several different ores. Thus much may be safely asserted, that if nickel, cobalt, and manganese are ever to be found in commercial zinc, they occur there accidentally, exceptionally, abnormally, and in quantities hardly to be appreciated, and utterly insignificant.

But few quantitative determinations of the impurities of zinc are recorded, but we can confirm the results we have obtained with Silesian zinc by referring to the previous analyses of German zincs by several chemists. Thus Wackenroder,\* in the memoir already cited, maintains that the principal impurities of Silesian zinc are lead, cadmium, and iron; and after him, Karsten draws the same conclusion from a considerable number of analyses of zincs from different works. In thirty-two analyses of Silesian zincs made by this eminent metallurgist, the amount of lead found varies from 0.24 per cent to 2.36 per cent.† A few other analyses we cite below.‡

\* *Ann. der Pharm.*, 1834, X. 53.

† *Archiv. f. Mineralogie*, Karsten u. Dechen, 1842, XVI. 597. Also in *Dingler's Polyt. Jour.*, 1842, LXXXVI. 193.

‡ An East-Indian zinc, which Bonnet analyzed, contained, in 100 parts, 0.43 of lead, and 0.24 of iron. *Ann. der Pharm.*, 1834, IX. 184. Jansen obtained a black residue weighing  $2\frac{1}{4}$  ounces from 8 pounds of Silesian zinc. He states the result of an analysis of the residue as follows. (*Ibid.*, 191.) The statement does not admit of any verification, is unintelligible and incredible.

Sulphate of Lead, . . . . .	985.77
Oxide of Cadmium, . . . . .	1.88
“ “ Copper, . . . . .	1.56
“ “ Iron, . . . . .	16.09
Carbide of Zinc, . . . . .	4.03
Silicium, . . . . .	13.77
Calcium, . . . . .	2.26
Residue of Sand and Carbon, . . . . .	13.00
	<hr/> 1038.36

Wittstein found in one sort of Austrian zinc as much as  $3\frac{1}{2}$  per cent of lead. Cited in *Ann. der*

*Carbon.* — With reference to carbon as an impurity of zinc, we have attempted to determine this single point, — Does it occur in the residue insoluble in dilute acids, as has been generally believed, but never to our knowledge proved? One fact alone renders the occurrence of carbon, or of any other non-metallic substance, in this residue extremely improbable. We have observed that the residues from the Silesian, New Jersey, Rousseau Frères, Berlin, and Mint zincs are completely dissolved in perchloride of iron, acidulated with chlorhydric acid. If carbon or silica were present in any appreciable quantity, complete solution of the residue in this reagent could not be expected. In testing the residues from our various spelters for carbon, we adopted the following process.

From thirty to forty grammes of the zinc to be tested were dissolved in pure dilute chlorhydric acid, the black residue thoroughly washed with hot water, and dried at a heat much below one hundred degrees. The dry, grayish powder was then ground up with fused chromate of lead, and the mixture was introduced into a small bulb, blown in a tube whose diameter was not quite a centimetre. At a short distance from the bulb, this tube was drawn down to a diameter of one or two millimetres, and the ex-

Pharm., 1836, XX. 179. Two other samples of Austrian zinc gave Wittstein, —

	(1.)	(2.)
Lead, . . . . .	0.27 per cent.	0.91 per cent.
Cadmium, . . . . .	0.23 “ “	0.16 “ “
Iron . . . . .	trace.	0.17 “ “

Otto's Lehrbuch der Anorganischen Chemie, Dritte Auflage, III. 139.

Jacquelain obtained from a specimen of French zinc, —

Carbon, . . . . .	0.003
Iron, . . . . .	0.142
Lead, . . . . .	0.685

Ann. de Ch. et Phys., 1843, [3.] VII. 203.

The following additional analyses are cited from B. Kerl's Handbuch der metallurgischen Hüttenkunde, Freiberg, 1855, I. 225. The original sources from which these determinations were derived by Kerl are not stated.

	Lead.	Iron.	Cadmium.	Carbon.
1. Belgian zinc (2d quality) . . . . .	0.4	0.4		
2. Silesian “ . . . . .	0.47	0.28	0.2 to 0.97	{ 0.04 0.75
3. “ “ . . . . .	0.15	0.32		
4. Iserlohn “ . . . . .	0.30	0.35		
5. “ “ . . . . .		0.25		0.41
6. Chinese “ (bad quality) . . . . .	0.80	1.50		
7. Lower Hartz zinc, . . . . .	0.85	0.73	(Also contains arsenic.)	

tremity of the fine tube placed under lime-water in a small test-glass. The bulb was heated till the chromate of lead was fused, and if any carbon had been present in the residue, the evolved gas would have caused a cloudiness or precipitation of carbonate of lime in the lime-water. In this manner we first tested our chromate of lead by itself, and found no cloud or precipitate in the lime-water. We next inserted the smallest possible particle of carbon into the bulb with a little chromate of lead, and obtained a large distinct cloud of carbonate of lime in the lime-water in the test-glass, and in the capillary tube which delivered the gas. Having thus proved the purity of the reagent employed, and the extreme delicacy of the test, we tested in succession the residues from Silesian, Vieille Montagne, and Berlin zincs, and from the zinc of Rousseau Frères. As precisely the same result was obtained with each of these zincs, it may be stated once for all.

On heating the mixture of residue and chromate of lead till the chromate fused, there appeared in each case a very slight deposit on the upper surface of the lime-water column in the fine tube. This deposit could not have been smaller and yet been visible; it was incomparably less than that produced by the atom of carbon which was purposely introduced into a similar tube, and was undoubtedly caused by the slight dust which collected on the residues during the processes of washing and drying, and which no possible precautions could entirely avoid. It is obvious from these experiments, that the often repeated statement, that the insoluble residue from zinc treated with dilute acids is carbon, rests on no adequate foundations, and that carbon is not an invariable constituent of crude zinc, as it is of iron. But on the other hand it is impossible to assert that carbon does not sometimes occur in commercial zinc as an accidental and wholly abnormal impurity. Thus in the specimen of New Jersey zinc which we examined, there were certain small cavities lined with black, as if a bubble of some carbonaceous gas had been decomposed within them, and the residue from this zinc, when tested as above described for carbon, produced a distinct cloudiness in the lime-water, which was sufficient evidence of the presence of a trace of carbon in this spelter; but the amount of this impurity was infinitesimal, and not at all to be compared in quantity with the lead and other metallic admixtures of which the residue mainly consisted. The presence of a little copper in this zinc may perhaps be connected with the occurrence of this trace of carbon. The residues from three of the English spelters also gave distinct reactions for carbonic acid in the lime-water; but, judging from the exceedingly small cloud of carbonate of lime produced, the amount of carbon in these zincs is even less considerable than that detected in the New Jersey zinc. The other English zinc (that from the works of Messrs. Vivian) yielded but the

merest trace of carbonate of lime, — a little larger deposit, perhaps, than that obtained from the Silesian, Vieille Montagne, and other zincs first experimented upon, but not more than may easily have been derived from the invisible dust which undoubtedly collected on the residue. From none of these zincs could we obtain nearly as much carbonate of lime in the test-glass as we got from the smallest possible atom of carbon heated with chromate of lead; and it is quite clear that there is never anything more than an infinitesimal amount of carbon in the considerable residue which remains when thirty or forty grammes of commercial zinc are dissolved in dilute acids.

Against the common opinion that carbon is one of the principal impurities of zinc, we would refer to the previously quoted statement of Wackenroder, who considered carbon only an accidental and mechanical impurity, and to the exact experiments of Karsten, who endeavored to determine the carbon in Silesian zinc by decomposing chloride of silver and chloride of copper by zinc, but “could find no trace of carbon in either the hard or the soft kinds of zinc.” \*

*Sulphur.* — It has been frequently stated that sulphur is a common impurity of zinc, and that it even occurs in the insoluble residue in combination with lead. We first tested the insoluble residue from Silesian zinc for sulphur, by dissolving about 30 grammes of the zinc in pure chlorhydric acid, separating the black residue, and dissolving it in pure nitric acid. It dissolved without any appreciable residue (another evidence of the non-existence of tin in this spelter), and the diluted solution gave no precipitate whatever with nitrate of baryta. With 40 grammes of Vieille Montagne zinc, we obtained precisely the same result. The Pennsylvanian zinc leaves no residue when treated with dilute acids, and is therefore free from lead, and certainly contains no carbon or sulphur which manifest themselves as an insoluble residue. The New Jersey zinc gave an exceptional result. The blackish residue, from 32 grammes of this zinc, could not be completely dissolved in boiling nitric acid. The partial solution gave no precipitate with nitrate of baryta; the undissolved portion was fused before the blow-pipe with carbonate of soda free from sulphur, and gave a distinct reaction, first for sulphur, and secondly for tin. The presence of tin in this spelter has already been demonstrated, and a minute trace of sulphur must also be counted among its impurities.

In addition to this negative evidence, that no precipitation is produced by barium salts in the diluted nitric acid solution of the residues from the various zincs, we would

\* Archiv. f. Mineralogie, Karsten u. Dechen, 1842, XVI. 607. Karsten also says: “I have cemented sheet zinc with coal for many days, and then melted it; but in the resulting mass of zinc I have found no trace of carbon.” Ibid., 608.

adduce positive experiments to show that any compound of sulphur with a metal, which might be present in the zinc, would, in all probability, be decomposed in presence of an excess of zinc and free acid.

Wackenroder, in the memoir already cited, distinctly states that the black residue from zinc is sulphide of lead, — a statement at first sight sufficiently plausible, but really inconsistent with the facts of the case. When precipitated sulphide of lead is mixed with a large excess of granulated zinc (Silesian, Vieille Montagne, or Pennsylvanian), and treated with moderately dilute sulphuric or chlorhydric acid, the black sulphide soon entirely disappears, while torrents of sulphuretted hydrogen are evolved. If, after all the zinc has been completely dissolved, the insoluble residue is fused before the blowpipe with carbonate of soda free from sulphuric acid, the mass thus obtained will not blacken silver.

If powdered galena be substituted for precipitated sulphide of lead, the same effects will be produced, though much more slowly. The sulphide of lead, therefore, suffers complete decomposition in presence of an excess of zinc and free acid, and it is of course absolutely impossible that this substance should be found in the insoluble residue.\*

The presence of sulphur in the insoluble residue from zinc is, without doubt, very rare ; but it is also an unquestionable fact, that a certain amount of sulphuretted hydrogen gas is generated whenever commercial zinc is treated with dilute acids. This phenomenon has been often observed. Thus Blancard† remarks, “that the sulphur often contained in commercial zinc may be shown by bringing paper wet with acetate of lead in contact with the gas developed therefrom.” Fordos and Gélis‡ say, that “the formation of this gas (sulphuretted hydrogen) can only be attributed to the partial reduction of the sulphuric acid by the nascent hydrogen.” Subsequently Jacquelain,§ doubting this supposed reduction of sulphuric acid, attributes the production of sulphuretted hydrogen to the presence of sulphurous acid or other compounds of sulphur,

\* We have observed that the sulphides of tin and copper are also decomposed when mixed with an excess of zinc and dilute acid. The sulphide of copper was rapidly decomposed, and the residue, after all the zinc had been dissolved, yielded only a very uncertain trace of sulphur before the blowpipe. Precipitated bisulphide of tin was decomposed much less readily, and when all the zinc had disappeared, the residue gave indications of sulphur before the blowpipe. Although this might have arisen from some impurity in the tinfoil from which the sulphide was prepared, yet it was evident that the decomposition of the sulphide of tin is effected with much greater difficulty than that of the sulphides of lead and copper.

† Jour. de Pharmacie, 1841, p. 543, in Dingler's Polyt. Jour. 1841, LXXXII. 425.

‡ Comptes Rendus, 1841, XIII. 437.

§ Ann. de Ch. et Phys., 1843, [3.] VII. 189.



with which the sulphuric acid is contaminated. Every specimen of zinc in our possession develops sulphuretted hydrogen when treated with dilute sulphuric or chlorhydric acid, as may be manifested by placing a slip of paper moistened with alkaline acetate of lead in the neck of the flask which contains the zinc and acid. But the question recurs, What is the source of the sulphur which is necessary for the generation of this gas? Is it contained in the zinc, or is it derived from the acids used in the experiment? To obtain a satisfactory solution of this problem, it is necessary to use an acid which does not contain sulphur in any form. Sulphuric acid will not answer the purposes we have in view in this experiment; for though it is undoubtedly possible to prepare sulphuric acid free from sulphurous acid, yet the doubt would still remain concerning the reduction of the sulphuric acid by the hydrogen, — a reduction not impossible at certain temperatures and in certain states of concentration. In testing for a minute trace of sulphur in zinc, it is evidently undesirable to employ a reagent which contains sulphur, in however stable a combination. Sulphuric acid being then excluded, will chlorhydric acid answer the purpose? It is easy to prepare chlorhydric acid which gives no precipitate with baryta salts, but it is very difficult to prepare this acid from common salt and sulphuric acid, so that, while containing no chlorine, it shall be absolutely free from sulphurous acid, or some lower compounds of sulphur. Loewenthal's\* test with sesquichloride of iron and ferricyanide of potassium will reveal the presence of such compounds of sulphur in chlorhydric acid, made with the utmost care, and in other respects pure. By means of chlorine or some similar oxidizing agent, these compounds of sulphur may undoubtedly be oxidized, or at least the larger part of these admixtures may be converted into sulphuric acid; whether their last traces can be oxidized in this way is a point by no means beyond a doubt. But if the chlorhydric acid has been treated with chlorine to accomplish this oxidation, it becomes necessary to remove from the acid the excess of the oxidizing agent, for sulphuretted hydrogen would not be developed from zinc, contaminated with sulphur, by an acid which contained free chlorine, or any substance of like properties. Thus common chlorhydric acid very often contains free chlorine, and no zinc will yield with such acid anything more than a very uncertain reaction for sulphur on lead-paper. To obtain chlorhydric acid which was above suspicion, and unquestionably free from every trace of sulphur, and from every oxidizing agent which might interfere with our reaction for sulphur in zinc, we found so difficult a task, that we finally rejected this acid altogether, and resorted to the following process. A solution of chloride of calcium, free from every trace of sulphur, was

\* Jour. pr. Chem., LX. 267.

first prepared by dissolving carbonate of lime in chlorhydric acid, adding ammonia in excess to the boiling solution, filtering off the precipitated oxides of iron and alumina, adding to the filtrate chloride of barium, and evaporating to dryness. The residue was dissolved in distilled water, and in this solution a slight excess of chloride of barium was present, as was proved by the precipitate produced by a solution of sulphate of lime. Oxalic acid free from sulphur was then prepared by the following process: a quantity of commercial oxalic acid was treated with enough cold water to dissolve about half of the acid taken, and the cold solution thus obtained was partially evaporated and crystallized; the mass of crystals was washed with a saturated solution of a portion of the crystals, and was finally dissolved in distilled water. In these two reagents, the chloride of calcium and the oxalic acid, so prepared, no sulphur could be detected, either by barium salts, Loewenthal's test, or by the blowpipe reaction on silver.

We applied to every zinc in our possession the following test for sulphur. 10 or 15 grammes of zinc were introduced into a small flask, and a portion of the solution of chloride of calcium and of oxalic acid added thereto; hydrogen gas was freely developed, and was tested for any sulphuretted hydrogen which it might contain, by placing a slip of paper moistened with alkaline acetate of lead in the narrow neck of the flask. In every case the paper was immediately and strongly blackened, showing conclusively that every one of the following zincs contains sulphur in a quantity extremely minute, but distinctly appreciable if a sufficiently delicate test be applied: —

1. Vieille Montagne zinc (in two distinct samples).
2. Silesian zinc.
3. The United States Mint zinc.
4. Pennsylvanian zinc.
5. Rousseau Frères zinc.
6. Berlin sheet zinc.
7. Silesian zinc (subjected to Meillet's \* process for purification from arsenic).
8. New Jersey zinc.
9.       “       “       (reduced by us from the New Jersey white zinc oxide).
10. English zinc (in four distinct samples).

These results are not in accordance with the statements of some previous observers. Thus Karsten, in the memoir previously cited, infers that sulphur is not contained in Silesian zinc, from the fact that he obtained no precipitate in passing the gas gen-

\* Dingler's Polyt. Jour., 1842, LXXXIII. 205, from Jour. de Pharmacie, 1841, 625.

erated by this zinc through a solution of acetate of lead. But it must be remembered, first, that we have no evidence that Karsten's acids were free from oxidizing agents, and secondly, that the reaction for sulphur on lead-paper is a more delicate test than any process of causing the gas generated to bubble through a liquid, even though the best form of apparatus be employed to secure as far as possible thorough contact of the gas with the fluid. Moreover, Karsten subsequently mentions that a delicate black precipitate is produced when the hydrogen from zinc is passed through nitrate of silver; this precipitate was probably sulphide of silver, and not metallic silver, as Karsten conjectured.

Again, Jacquelain, in the memoir already referred to, concludes that sulphur was not contained in the specimen of French zinc which he examined, because a complete solution of the zinc in aqua regia gives no precipitate with chloride of barium. But obviously the precipitation of sulphate of baryta in aqua regia is by no means a sufficiently delicate test for an amount of sulphur at best exceedingly minute. In the same paper, Jacquelain, criticising the observation reported by Fordos and Gélis of the generation of sulphuretted hydrogen from zinc and dilute sulphuric acid, implies that there is no sulphur in zinc by stating that the development of sulphuretted hydrogen from zinc may be avoided by using properly prepared acid. The acid which Jacquelain used had been saturated with chlorine gas, in a process of which the principal object was the purification of the sulphuric acid from sulphurous acid. That this acid occasioned no development of sulphuretted hydrogen from the zinc is not to be wondered at, but it is not to be argued from this fact, that there is no sulphur in zinc. With regard to sulphur in the zinc from New Jersey, Alger\* has remarked that the New Jersey zinc ore is known to contain no sulphur; but, on the other hand, Jackson† observed the sulphuret of zinc in the mine of red oxide of zinc in Franklin, Sussex County, New Jersey, and a simple experiment demonstrated to us the existence of sulphur in that ore. 10 or 15 grammes of the red oxide of zinc, not entirely free from the gangue of carbonate of lime in which the ore occurs, were reduced to a fine powder, and treated with moderately dilute pure sulphuric acid. A vigorous evolution of sulphuretted hydrogen was the immediate result.

*Arsenic.*—The general opinion that arsenic is a very common impurity in commercial zinc may, we think, be traced back to the confident assertion of Proust, near the beginning of this century, afterwards extensively copied and generally believed. But it is quite clear that Proust, and probably many other of the early chemists, were led

\* Am. J. Sci., XLVIII. 253.

† Proc. Am. Association, 1850, IV. 336.

into error by the close external resemblance of the sulphide of arsenic to the sulphide of cadmium, which last metal, not recognized till 1817, has since been shown to be a very common admixture in the zinc of commerce. The invention of Marsh's apparatus, in 1835, gave to chemistry a test for arsenic of most wonderful delicacy; and Marsh\* himself, in his original memoir, describing his process, remarks, that "the only ambiguity that can possibly arise in the mode of operating above described, arises from the circumstance that some samples of the zinc of commerce themselves contain arsenic." But Marsh, thus careful to suspect his zinc, says not a word about the purity of his acid, and many observers since Marsh have been more ready to attribute the infinitesimal trace of arsenic, which his process has enabled them to detect, to the zinc, than to the acids they have used. Schaeffele† has actually attempted to determine quantitatively the per cent of arsenic present in French, Silesian, and Vieille Montagne zincs, and his results have been quoted in many recent handbooks and treatises on toxicology.

The conclusions at which we have arrived, after a long course of experiments with many different zincs, and various acids, are these:—first, that much of the zinc of commerce is free from arsenic, or at least contains no arsenic that can be detected by the most delicate tests known for that metal; secondly, that the sulphuric and chlorhydric acids found in commerce do very often contain arsenic, and are always so liable to contain it as to be utterly unfit for use in Marsh's process without special purification for that purpose. The steps by which we were led to these results, and the evidence on which they are founded, we proceed to describe. We have used exclusively Marsh's process for the detection of arsenic, applied with the apparatus and with all the precautions recommended by Otto.‡ Our apparatus consisted of a flask provided with a funnel-tube, and a tube bent at right angles, with which were connected by connectors of sheet India-rubber, first, a tube of the form of a chloride of calcium tube, filled with asbestos; secondly, a similar tube, filled with pumice-stone soaked in caustic potassa; and thirdly, one filled with chloride of calcium. Through these three tubes, in the order in which they are named, the gas generated in the flask was obliged to pass before it arrived at the reduction-tube, which was of hard German glass, and about one centimetre in diameter. The reduction-tube was drawn

\* Edinburgh New Phil. Jour., XXXV. 235.

† Extract from a thesis presented by M. Schaeffele. Jour. de Chimie Médicale, [3.] VI. 173; also in Dingler's Polyt. Jour., 1850, CXVI. 248.

‡ A Manual of the Detection of Poisons. Translated from the German by Elderhorst. New York: Baillière. 1857.

down to a fine bore, and during the progress of an experiment was heated by one of Bunsen's triple gas-burners. To prevent any elevation of the temperature in the flask during an experiment, it was immersed in cold water, and the dilute acid used was always cold, and added in small quantities. With this apparatus (which for convenience we shall designate as Otto's apparatus), taking every possible precaution to insure its perfect cleanness, we made several experiments upon Silesian zinc. 200 grammes of this spelter, carefully granulated, were used in each experiment, and the sulphuric acid employed was a commercial acid made in this country from Sicily sulphur. We were not unaware of the fact, that arsenic is almost invariably found in the foreign sulphuric acid made from various impure sulphurs of unknown origin, or from pyrites;\* but it is a common impression that the American acid manufactured directly from Sicily sulphur is free from arsenic. Positive statements to this effect have been made by chemists who have had mainly in view the common use of sulphuric acid in the preparation of chemical compounds used in pharmacy, and the assertion has enough plausibility to command ready and general belief. Using such acid and 200 grammes of granulated Silesian zinc, we obtained, at the end of the hour during which the reduction-tube was heated, a deposit of arsenic perfectly distinct, though not bright enough to be called a mirror. Our next experiment was made with the same acid upon 200 grammes of an excellent sample of Vieille Montagne zinc, perfectly clean and carefully granulated. At the end of the hour during which the gas was passed through the reduction-tube, a brownish, volatile coating was found in that part of the tube where the bore was smallest. These experiments on Silesian and Vieille Montagne zincs were several times repeated, and always with the same result; the deposit in the reduction-tube was often too thin and slight to be positively identified as arsenic, but it could not be distinguished from the deposit of that metal, and would have been perfectly fatal in a medico-legal investigation, or in any case in which absolute purity of

\* On the subject of arsenic in foreign sulphuric acid, the following authorities may be referred to:—

Martius, Schweigger's Jour. f. Ch. u. Phys., 1811, III. 363.

Wackenroder, Ann. der Pharm., 1834, XII. 189.

Wackenroder, Ann. der Pharm., 1835, XIII. 241.

Vogel, Jour. f. pr. Ch., 1835, IV. 239.

Ficinus, Ann. der Pharm., 1835, XV. 77.

Berzelius, in his Jahres-Bericht, 1841, XX. 192.

Brett, Philosophical Mag., 1842, [3.] XX. 404.

Schnedermann and Wöhler, Jour. f. pr. Ch., 1845, XXXV. 186.

Dupasquier, Comptes Rendus, 1845, XX. 794.

Cameron, Chem. Gazette, No. 320, p. 75, in Jour. f. pr. Ch., 1856, LXVIII. 64.

the materials was desired. Not convinced that the zincs were the source of the arsenic, we desired to prepare a quantity of sulphuric acid in which the presence of arsenic could not possibly be suspected. To attain this object, we subjected a specimen of American sulphuric acid to the following process. The acid was first boiled with a little flowers of sulphur, as proposed by Barruel,\* in order to free it from the nitrous fumes which the common sulphuric acid almost always contains; a small quantity of pure chlorhydric acid was then stirred into the cooled acid, which had been carefully decanted from the free sulphur, and the whole again boiled; to the acid, again cooled, a second addition of chlorhydric acid was made, and again the acid was heated till dense white fumes had been escaping for upwards of half an hour. During this process, the volatile chloride of arsenic is completely driven off, the second addition of chlorhydric acid being made, as has been recommended by H. Rose,† in order to insure this result. Lastly, a portion of chlorine-water was added to the cooled acid to oxidize any sulphurous acid which might be contained in it, and after a third boiling, the acid, cooled and diluted with three parts of water, was ready for use. This method of purifying sulphuric acid is a combination and modification of several well-known processes. Buchner‡ has described in full the process of purifying sulphuric acid by means of chlorhydric acid, and the use of chlorine as above described was recommended by Jacquelin.§ The whole operation can be performed in a shallow evaporating-dish, and presents no serious difficulties of any kind. With the acid thus prepared, we tested 200 grammes of Vieille Montagne zinc, and after passing during more than an hour a continuous, gentle stream of gas through the reduction-tube, of which about four centimetres were maintained at a bright red heat, we found that there was absolutely no deposit whatever in the cool and narrow part of the reduction-tube. With the same acid and apparatus, 200 grammes of Pennsylvanian zinc (which had been proved to be altogether the purest zinc in our possession) gave absolutely no deposit of any kind in the fine reduction-tube at the end of one hour, the time during which, in all our examinations for arsenic, we maintained a steady flow of hydrogen through the red-hot reduction-tube. We had now demonstrated that two different spelters, of which we were fortunate in possessing considerable quantities, were free from arsenic, or, more strictly, that in the given quantities of metal, and in the stated times, Marsh's infinitely delicate test could not detect arsenic in these two zincs. It was also rendered

\* Dingler's Polyt. Jour., 1837, LXIV. 55; from Jour. de Ch. Médicale, 1836, No. 4.

† Pogg. Ann., 1858, CV. 571.

‡ Ann. der Ch. u. Pharm., 1855, XCIV. 241.

§ Ann. de Ch. et Phys., 1843, [3.] VII. 191.

very probable that the sulphuric acid with which we first experimented contained arsenic, inasmuch as we had obtained a distinct deposit of arsenic from that acid and the Vieille Montagne zinc, which subsequent experiment had proved to be free from that impurity. In order satisfactorily to establish these conclusions, it was necessary to prove by frequent repetition that the same result might always be expected from these two zincs, and that their freedom from arsenic was a property shared by the whole sample, and not an accidental peculiarity of a particular fragment. At sundry times we therefore repeated again and again the long and careful test for arsenic above described with these two samples of spelter, and invariably arrived at the same conclusion; namely, that no deposit of any kind could be obtained in the reduction-tube from these zincs and purified sulphuric acid.

*Delicacy of the Test.* — To prove the sufficiency of our apparatus, and the absence of every substance which might be supposed to prevent the formation of the arsenic mirror, and, moreover, to obtain mirrors from known quantities of arsenic with which roughly to compare deposits obtained in experiments in which the arsenic was the unknown quantity, we made the following experiments: —

1. 200 grammes of Vieille Montagne zinc, about 200 c. c. of purified dilute sulphuric acid, and 20 drops of pure chlorhydric acid, were first thoroughly tested for arsenic, and found to be perfectly pure.

2. 200 grammes of Vieille Montagne zinc, and about 200 c. c. of purified sulphuric acid, were thoroughly tested, and gave no deposit in the reduction-tube. Into the flask whose contents had been thus proved, two tenths of a milligramme of arsenious acid (weighed on a Plattner's assay balance, made by Lingke of Freiberg), dissolved in 20 drops of the same chlorhydric acid used in the first experiment, were introduced. An enormous mirror of arsenic appeared instantly in the reduction-tube. To get the greatest effect, the arsenious acid should be thoroughly dissolved, and its solution should be effected without the use of any but a very gentle heat.

3. Using the same zinc and the same acids, in the same quantities which were employed in the foregoing experiments, and proving the materials as in the last experiment, we obtained, in half an hour, a very large and distinct mirror of arsenic, by introducing into the flask one tenth of a milligramme of arsenious acid.

4. 200 grammes of Pennsylvanian zinc and about 200 c. c. of purified sulphuric acids were tested for one hour, and proved to be perfectly pure. One milligramme of arsenious acid had been dissolved in 20 drops of the pure chlorhydric acid which had been used in the first experiment, and the solution diluted with distilled water to the bulk of 50 c. c. One cubic centimetre of this solution was introduced into the flask whose

previous contents had been proved as above described, and at the end of three quarters of an hour a distinct deposit of arsenic was found in the reduction-tube. The amount of arsenious acid actually placed in the flask was two hundred-thousandths of a gramme (.00002 gram.).

0.00002 gram. arsenious acid = 0.000015 gram. arsenic.

Ratio of the arsenic present to the zinc =  $0.000015 : 200 = \frac{75}{1,000,000,000}$ .

“ “ “ “ “ amount of liquid in the flask = about  $\frac{75}{1,000,000,000}$ .

Our apparatus was therefore competent to detect a quantity of arsenic less than one ten-millionth of the weight of the zinc used, or of the amount of fluid in the flask. This quantity of liquid necessarily varied somewhat, in consequence of the slight additions of acid necessary to maintain a constant current of hydrogen, but only varied to be increased, never diminished. Remembering the wide limits of error in many chemical processes, the comparative coarseness of most chemical tests, and the many unavoidable inaccuracies in weighing and measuring, is not the assertion perfectly safe, and in strict conformity with the general use of language in other qualitative or quantitative determinations, that a specimen of zinc is free from arsenic, which does not show the slightest trace of that metal in an apparatus abundantly capable of detecting the ten-millionth part of arsenic? We are aware that this is not the limit of delicacy\* of Marsh's test, but, assured of this delicacy, we rest satisfied with it as sufficient for our present purpose. The more delicate the test, the stronger is our present argument, and the greater need is there of exceeding caution in applying this test in the investigations of medico-legal or pharmaceutical chemistry.

In connection with these experiments on the delicacy of the test, we would call attention to the fact, that the sulphuretted hydrogen, which we have shown in our examinations for sulphur to be always developed from commercial zinc, does not prevent the exhibition of such a very small amount of arsenic as 0.000015 gram. Chevallier,† and more recently Blondlot‡ and Leroy,§ assert that the presence of the insoluble sulphide of arsenic cannot be recognized by Marsh's test, and that arsenic may therefore be concealed by being converted into the sulphide. This is the natural and general

\* M. Signoret (Taylor on Poisons, 2d Edition, 1859, London, p. 396) states that he has procured metallic deposits with only the 200,000,000th part of arsenic in the liquid; but it is not clear from such a statement what the exact amount of arsenic in the apparatus was which enabled him to obtain deposits,—a very material point.

† Jour. de Ch. Méd., [2.] V. 380, in Berzelius's Jahres-Bericht, 1841, XX. 192.

‡ Comptes Rendus, 1857, XLIV. 1222.

§ Ibid., 1859, XLIX. 469.



opinion, though Marsh, in his original memoir, distinctly says, that "the presence of arsenic in artificial orpiment and realgar, . . . . and in sulphuret of antimony, may be readily shown by this process, when not more than half a grain of any of those compounds is employed." \* When the amounts of arsenic and of sulphuretted hydrogen are alike minute, it is quite certain that the reaction for arsenic is not affected by the unavoidable presence of this gas.

*Arsenic in American acids.* — We have tested four different kinds of American sulphuric acid, of which two were commercial oil of vitriol, and two were sold as chemically pure acids. The test applied to these acids was always the same, and may be described once for all. 100 grammes of Pennsylvanian zinc, from the same bar which in many trials had been shown to be free from arsenic, was placed in the flask, and the acid to be tested was used instead of the purified acid which was always employed when the zinc was the suspected substance. In every experiment, the gas was passed through the reduction-tube at least one hour. In experiments several times repeated, the sulphuric acid made at Providence, Rhode Island, invariably yielded a distinct deposit in the narrow part of the tube. It should be stated, however, that the Providence acid used in these repeated experiments all came from one carboy. In a sample of the acid manufactured at Waltham, Massachusetts, we detected a similar trace of arsenic. The deposits obtained from these two acids were hardly larger than that produced by the 0.000015 gram. of arsenic used in the fourth experiment on the delicacy of the reaction, but, on the other hand, only a small quantity (from 25 to 50 c. c.) of the acid could be employed in a single experiment.

The arsenic which is eliminated from these acids during the process of purification with chlorhydric acid may easily be collected, and exhibited by Marsh's test. For this purpose, the sulphuric acid should be heated with the chlorhydric acid in a flask or retort, from which the gas generated is conducted into a small quantity of distilled water, kept constantly cool. The volatile chloride of arsenic condenses in the water, and the arsenic in the solution is readily manifested in Otto's apparatus. The chlorhydric acid used in this experiment must be absolutely free from arsenic; such acid may be obtained by passing sulphuretted hydrogen through chlorhydric acid prepared from salt and pure sulphuric acid. Moreover, the sulphuric acid in the flask or retort must be kept fuming during at least half an hour, in order to secure the complete volatilization of the chloride of arsenic.

The chemically pure sulphuric acid, so called, manufactured by Rosengarten, of

\* Edinburgh New Phil. Jour., XXXV. 235.

Philadelphia, was purer than the commercial acid with reference to arsenic as well as to lead; indeed, in one experiment it yielded no sensible deposit in the reduction-tube, but in several subsequent experiments with pure zinc, in which we attempted to use Rosengarten's acid instead of that purified by ourselves, we obtained faint deposits which precluded its use, and showed it to be untrustworthy in such delicate examinations for arsenic by Marsh's process. To the "chemically pure" sulphuric acid made by Powers and Weightman of Philadelphia, precisely the same remarks apply; it is unfit for use in any research where scrupulous accuracy is necessary, and of which the results are worse than worthless if they be not certain and impregnable. It may be granted that the amount of arsenic in any small quantity of these acids is really too minute to be of any consequence, except in the most refined experiments. On the other hand, it must be remembered that in some pharmaceutical processes, and in many chemico-legal examinations for arsenic, in which a large amount of acid is often necessarily used, the whole of the arsenic contained in the reagents employed is, by the very nature of the process, concentrated and condensed into a very small compass. For example, in a poisoning case in which the chemist is obliged to destroy by acids any considerable portion of the body, as is often the case, it may be necessary to use many pounds of sulphuric or chlorhydric acid, and the very care and pains with which the chemist labors to concentrate every grain of arsenic in that organic matter into the small glass of liquid, which he finally tests by Marsh's process, also concentrates into the same glass all the arsenic contained in all the reagents which he has employed in the whole process. Under such circumstances the existence of *any* arsenic in sulphuric acid, capable of exhibition from a few cubic centimetres of the acid, becomes a fact of the utmost moment. From neglecting this arsenic in sulphuric acid arose the long controversy concerning normal arsenic in the animal body. To the objection that Marsh's test is too delicate, and that we should find all the elements everywhere if we had for each of them a test as refined as Marsh's for arsenic, it may be replied, first, that Marsh's process is not thought too delicate to base vital conclusions upon in difficult examinations for arsenic in poisoning cases, and secondly, that facts are not to be met by a theoretical objection, which is at any rate purely speculative, and furthermore is no objection if, as is certainly possible, the theory be true.

We are aware of the common opinion, that sulphuric acid made from Sicily sulphur contains no arsenic,\* and we do not propose to explain the source of the arsenic found

\* For a strong statement of this opinion, see Ure's Dictionary of Arts, &c., 4th edition, Boston, 1853, Vol. II. pp. 791, 799.

in American sulphuric acid, further than to suggest that its presence seems not unnatural when we remember that the sulphides of arsenic are often associated mineralogically with the sulphur from which the acid is made. Long ago Pfaff,\* in commenting upon the observation made by Martius of arsenic in sulphuric acid, said that the sample analyzed by Martius was probably made from sulphur containing orpiment or realgar, minerals which are found with sulphur in the solfataras. Stromeyer † detected arsenic in the mixture of sal-ammoniac and sulphur, which is one of the many volcanic products of the Lipari Islands, and there seems to be no good reason for supposing that the sulphur, which is exported from the same locality, would escape contamination with arsenic. Daubrée ‡ has remarked that arsenic, as sulphide, occurs in the fissures of the lavas at Etna, at Vesuvius, and at the solfataras of Pouzzoles and of Guadeloupe. Scacchi§ also states, that among the substances found in the fumaroles of the solfataras are pyrites, realgar, mispickel, and dimorphine. Orfila,|| and before him Vogel, of Munich, imply that the leaden chambers in which sulphuric acid is made communicate arsenic to the acid.

Whatever we have said with regard to the American sulphuric acid, applies with still greater force to the commercial chlorhydric acids. That common chlorhydric acid contains chloride of arsenic, is a fact which was long ago observed, and has been fully discussed by Wackenroder,¶ Dupasquier,\*\* Otto,†† and many others.‡‡ We have examined two different samples of chlorhydric acid made in this country. Dilute chlorhydric acid, instead of sulphuric, was used in Marsh's apparatus with 200 grammes of pure Vieille Montagne zinc, and before the hydrogen generated had been passing through the heated reduction-tube fifteen minutes, there appeared in the fine part of the tube a brown deposit, which in an hour increased to a large and distinct mirror of arsenic, readily verified by other tests. Both samples of acid gave the same result, and we may add that, even on a small scale, we found great difficulty in preparing from salt and sulphuric acid a specimen of chlorhydric acid perfectly free from arsenic. The thorough purification of the acid by means of sulphuretted hydrogen, as recommended

\* Schweigger's Jour. f. Ch. u. Phys., 1816, XVIII. 283.

† Ibid., 1825, XLIII. 452.

‡ Ann. des Mines, [4.] XIX. 680.

§ Journal f. pr. Ch., 1852, LV. 54.

|| Ann. d'Hygiène Publique, XXII. 408.

¶ Ann. der Pharm., 1835, XIII. 241.

\*\* Comptes Rendus, 1841, XIII. 630.

†† Ann. der Ch. u. Pharm., 1856, C. 39.

‡‡ See also Ure's Dictionary of Arts, &c., 4th edition, (Boston, 1853,) II. 248, Art. *Muriatic Acid*.

by Otto, is therefore an absolutely necessary preliminary to the use of chlorhydric acid in any examination for arsenic.

From the examination of so few samples of sulphuric and chlorhydric acids, we do not pretend to have established the affirmative proposition, that there is always arsenic in these acids; their impurity was only an incidental difficulty in this research, and we strayed thus far from our main subject, only because of the great importance of trustworthy information upon this point to the pharmacist, and to the chemist who has to do with poisoning cases. Our observations, in connection with the facts long since established regarding the contamination of foreign sulphuric and chlorhydric acids with arsenic, may well lead the pharmacist and the analytical chemist to distrust his acids, till accurate experiments have proved them to be above suspicion; and we believe that careful investigations will hereafter show that arsenic is introduced into pharmaceutical preparations by the acids employed in their manufacture to an extent far greater than would now be credited. The task of the chemist who is called upon to examine a human body or organs of the body for arsenic, is a simple one when the poison is found in its original condition, unabsorbed and unaltered, but in difficult investigations of this kind, when the poison has been absorbed and diffused through a large mass of organic matter which must be destroyed by acids, the precautions insisted upon by Gaultier de Claubry,\* and by Galtier,† and other modern toxicologists, should be strictly observed. Not only should all the reagents to be employed be thoroughly tested *à blanc*, but furthermore, an experiment parallel with the actual examination of the suspected organic substances should be carried on with the same reagents in the same quantities, in a similar apparatus, and in all respects under like conditions, upon a quantity of normal animal matter equal to the weight of the suspected substances. In this way only can the chemist avoid the fatal uncertainty consequent upon the employment, in large quantity, of reagents whose purity is not above suspicion.

We return to the examination of other zincs for arsenic. With the same purified acid used in our previous experiments on Pennsylvanian and Vieille Montagne zincs, we tested 200 grammes of *Silesian* zinc, carefully granulated, and perfectly clean. For half an hour, the hydrogen passed steadily through the red-hot reduction-tube without leaving the slightest deposit in the fine tube beyond the heated portion, but on con-

\* Briand, et Chaudé, et Gaultier de Claubry, Manuel complet de Médecine Légale, 5<sup>me</sup> édition, (Paris, 1852,) p. 752.

† C. P. Galtier, Traité de Toxicologie, (Paris, 1855,) Tom. I. p. 362.

tinuing the operation beyond this time (indicated by Otto as sufficient for the testing of the materials *à blanc*), a faint but perceptible mirror gradually formed. This result indicates, first, that this sample of Silesian zinc was not perfectly free from arsenic, and secondly, that it is dangerous to conclude that the zinc and acid, which have given no reaction for arsenic during half an hour in Otto's form of Marsh's apparatus, will therefore give no mirror in the next half-hour, even though no arsenical compound be added to the apparatus. In any delicate examination for arsenic, this is a point to be carefully borne in mind. Our results with this zinc were corroborated by several similar experiments.

The zinc of Rousseau Frères was next submitted to the same test, with the same acid. 75 grammes of this zinc yielded in half an hour a brown deposit, hardly to be called a mirror, although covering a considerable portion (2 centimetres) of the tube. The final result of the experiment was not distinguishable from the result of the test of Silesian zinc.

With the same acid and apparatus, 200 grammes of New Jersey zinc gave a distinct mirror of arsenic, so large in amount, that the arsenic could be easily recognized by its characteristic odor. The mirror began to form at once, and gradually increased during the hour, which was the duration of the experiment.

Having at hand a quantity of the ore from which this zinc is extracted, we extended our search for arsenic to the red oxide of zinc, which is the source of this spelter. Several grammes of the red oxide, finely powdered, were moistened with 30 drops of pure nitric acid, and treated with a measured quantity of pure chlorhydric acid, prepared from common salt and sulphuric acid free from arsenic. The solution, with the very slight residue, was then gently evaporated to a small bulk, with a small measured quantity of Rosengarten's sulphuric acid. The imperfect solution thus prepared was introduced into the flask of our apparatus, whose previous contents of zinc and acid had been thoroughly tested for one hour, and found perfectly pure. In ten minutes a distinct deposit of arsenic was obtained, which in half an hour increased to a large and unmistakable mirror. To prove beyond a doubt that this arsenic came from the oxide of zinc, and not from the acids employed in preparing the solution, we tested in a clean apparatus with fresh zinc and acid, which had been proved pure by a test of one hour in duration, the same quantities of the same acids evaporated together as in the experiment above described. At the end of one hour (the second hour during which the apparatus had been at work) a deposit, perceptible on close inspection, was discovered in the narrow part of the reduction-tube. This deposit was invisible on any cursory examination, and bore no comparison with the very decided mirror of

arsenic obtained in the previous experiment. In two other similar examinations of the red oxide of zinc, we obtained the same strong evidence of the presence of arsenic in this ore, and the associated mineral, Franklinite, yielded, in the single careful test to which we subjected it, a mirror of arsenic sufficient to give the smell and all the other characteristic reactions for arsenic. To obtain satisfactory results, the solution of the oxide must never be heated above  $100^{\circ}$ , and the small quantity of nitric acid which is used to facilitate solution must be completely driven off before the liquid is introduced into the apparatus.\*

If any further evidence of the presence of arsenic in the New Jersey spelter and its ore were needed, it might be found in the following experiment with a zinc which we ourselves prepared by reducing the New Jersey white oxide of zinc with charcoal, in a refractory retort such as are furnished by the dealers in chemical apparatus at Paris. 20 grammes of this zinc, tested in Otto's apparatus with purified sulphuric acid, yielded in five minutes a distinct deposit of arsenic, and in half an hour a large mirror.†

\* We have also found arsenic in no inconsiderable quantity in the white zinc oxide, prepared from this ore for use as white paint. Two different samples, bought of authorized dealers, yielded large mirrors of arsenic, many well-marked spots on porcelain, and other of the reactions for arsenic. Moreover, a large precipitate of sulphide of arsenic was produced by sulphuretted hydrogen in their solutions. The qualitative examination of these two samples showed also the absence of lead and copper, and the presence of distinct traces of cadmium, iron, tin, and perhaps of antimony. It has been supposed that the superior quality of the French white zinc oxide was attributable to the presence of sulphur in the American article. To settle this question, we have determined, in two samples of New Jersey white oxide of zinc, the amount of matter insoluble in chlorhydric acid, and the per cent of sulphuric acid which they contained.

	I.	II.
Matter insoluble in chlorhydric acid, . . . .	0.0006 per cent. . . . .	0.00033 per cent.
“ “ “ sulphuric acid, . . . .	0.417 “ . . . .	0.361 “

These impurities are obviously too insignificant to account for the difference between the American and the French zinc-white, a difference probably due to the different mechanical conditions in which the oxide is obtained by the different processes employed in this country and in France. In a letter from Mr. John M. Ordway, we have the results of examinations of these paints made by this chemist in 1855: “The French oxide when dissolved in chlorhydric acid left a little coarse dirt; the colorless solution treated with ammonia in excess gave a very slight white precipitate, soluble in potash and in acids, perhaps alumina. There was also a very faint trace of iron and of sulphuric acid. The American oxide afforded a somewhat colored solution, a little fine soot remaining undissolved. The solution gave a brown precipitate of peroxide of iron when treated with ammonia, and also yielded a considerable precipitate with chloride of barium.”

† A further qualitative examination was made of this zinc, as follows. About 10 grammes were dissolved in pure chlorhydric acid; a considerable black residue remained, which was separated, dissolved in nitric acid, and the solution evaporated nearly to dryness. The flocculent precipitate which separated was filtered off and fused before the blowpipe with carbonate of soda which contained no metal. Ductile spangles were obtained,

To ascertain whether the Pennsylvanian and Vieille Montagne zincs were always free from arsenic, we procured and tested another sample of the zinc manufactured at the Pennsylvania and Lehigh zinc works, and a second sample of Vieille Montagne spelter. The Pennsylvanian zinc was, as before, remarkably free from lead, leaving no residue when dissolved in dilute sulphuric acid; but on testing 200 grammes of it in Otto's apparatus with purified acid, it gave in half an hour a slight deposit in the reduction-tube, which in an hour increased to a distinct brown coating. A similar result we obtained in testing the second sample of Vieille Montagne zinc; 200 grammes of it with pure acid yielded a deposit in the reduction-tube, fatal to its use in any delicate experiments. It should be stated, that the external appearance of this spelter indicated very clearly that its quality was inferior to that of the sample first examined. It is obvious from these results, that zinc manufactured in the same works, and from the same ore, may not always contain the same impurities, or rather that it never is to be expected to contain the same percentages of the same impurities. From the nature of the process of reduction, it would naturally be the case that the more volatile impurities should be present in the zinc which distils first in greater quantities than in the zinc which is reduced from the last part of a given charge of ore. Thus it is easy to imagine that the zinc which comes over first should be contaminated with arsenic, while that which is last reduced might be perfectly free from that impurity. The same principle explains the variations in the amount of cadmium contained in different samples of the same spelter, and indeed accounts in great measure for the varying per cents of all the impurities found in different specimens of any zinc, though made by the same process from the same ore.

which on solution in chlorhydric acid, and treatment with terchloride of gold, gave the reaction for tin. To the filtrate from the precipitate just mentioned, pure dilute sulphuric acid was added, and an abundant precipitate separated at once; this precipitate, reduced on charcoal with carbonate of soda, gave a large button, which was dissolved in nitric acid, and tested with chromate of potassa, a voluminous precipitate of chromate of lead separated immediately. No traces of copper were detected.

About 250 grammes of the oxide of zinc had been placed in the retort in which the reduction was to be effected, but only about 50 grammes of zinc were obtained, because the experiment was prematurely ended by the melting of the retort, caused by a combination of the oxide of zinc with the silicates of which it was made. These 50 grammes were only a fourth of the quantity of zinc which 250 grammes of the oxide should yield, and it is interesting to observe that lead and tin, as well as arsenic, accompanied this early product of the distillation. The source of this lead is uncertain; it is not inconceivable that the glaze of the retort should contain it, though to all appearances it was not a lead glaze; but the fact that lead was found in these first portions of the distilled zinc is perhaps none the less interesting, if it did come from the retort. The process of preparing pure zinc by reduction from the oxide on a small scale, is at best very laborious and uncertain. (Compare Neumann in the Abridgment of his Chemical Works by Lewis, London, 1759, p. 116.)

Lastly, we submitted our four specimens of English zinc to the test for arsenic. With purified acid, 200 grammes of the zinc made by Dillwyn and Company began to show a deposit in the reduction-tube within ten minutes of the commencement of the experiment, and in twenty-five minutes this deposit increased to a very perceptible mirror. A similar result was obtained from 200 grammes of the Mines Royal zinc. In fifteen minutes the stream of hydrogen from this zinc began to deposit arsenic in the reduction-tube, and at the end of three quarters of an hour, a thin but perfectly distinct mirror extended over three or four centimetres of the fine tube. On the label which accompanied the specimen of the spelter made at Minera, near Wrexham, it was stated that the zinc was manufactured from silicate of zinc, and we therefore expected to find this spelter purer than the ordinary English zinc made from blende; but, on the contrary, it contained a large amount of lead, and the test for arsenic showed it to contain more of that impurity than either of the two specimens before examined. 100 grammes of the Wrexham zinc began to show a deposit in the reduction-tube in ten minutes from the beginning of the experiment, and at the end of an hour a mirror had accumulated large enough to be identified by the arsenical odor. But of the four samples of English zinc, that of the Messrs. Vivian contained the most arsenic; 200 grammes of this spelter yielded an enormous mirror of arsenic in less than ten minutes, and in a few minutes more a second mirror, large enough to give the characteristic odor. With regard to English zinc, therefore, our observations do not agree with those of Brett,\* who states that he has examined many specimens of English and foreign zincs, and could never obtain any indications of arsenic when the sulphuric acid was pure. The explanation of this discrepancy is to be found in the fact, that the test applied by Brett, although essentially Marsh's test, had not the extraordinary delicacy which is insured by Otto's form of Marsh's apparatus.

This question now suggested itself: In presence of an excess of zinc, is not arsenic retained in the black residue (lead) from zinc dissolved in dilute acids, in such a condition, that it is not attacked by the acids or by the hydrogen, and therefore escapes detection? To determine this point, if possible, we dissolved 40 grammes of the *Vieille Montagne* zinc, which had showed no trace of arsenic by Marsh's test in dilute sulphuric acid, free from arsenic. The residue obtained was washed, treated with chlorhydric and a few drops of nitric acid, and the solution gently evaporated to a small bulk in presence of a little pure sulphuric acid. The mixture thus obtained was washed into the flask of Otto's apparatus, whose previous contents of zinc and acid had

\* *Philosophical Magazine*, 1842, [3.] XX. 404.



been thoroughly tested *à blanc* and found pure. At the end of the second hour, a very slight deposit was discernible on close inspection in the fine tube, but the result was too doubtful to warrant the assertion that arsenic was contained in the insoluble residue. We next tried the same experiment with Silesian zinc, in which Marsh's test had detected arsenic. The residue from 40 grammes of this zinc, submitted to the process just described, produced in the reduction-tube in fifteen minutes a brown deposit, which in half an hour became well marked, and at the end of the hour afforded sufficient evidence of the presence of arsenic in the residue, it being well understood that the zinc and acid used in this experiment had been previously tested for one hour and found pure. The only conclusion to which these experiments point is, that when a given sample of zinc contains arsenic, a portion of that arsenic will escape combination with the hydrogen generated by the solution of the zinc, and will remain in the insoluble residue. It was useless in this connection to examine the residue from New Jersey zinc, because that spelter itself contained arsenic, and its residue contained metallic copper, which would inevitably retain arsenic, as in Reinsch's test. The Pennsylvanian zinc gave no residue with acids.

The absolute necessity of obtaining a zinc free from arsenic for many chemical investigations, renders any process for purifying zinc from arsenic a matter of considerable interest and importance. We therefore tried the process of purifying zinc by fusing it with one fourth of its weight of saltpetre, a method fully described by Meillet,\* but previously suggested by Orfila.† 760 grammes of Silesian zinc were finely granulated and mixed with one fourth this weight of saltpetre, by placing the zinc and nitre in alternate layers in a Hessian crucible. The mixture was heated till deflagration ensued, when the melted mass was poured into cold water to separate the slag, caustic potassa, and any arseniate of potassa which might have formed. The washed mass was remelted, and again granulated. The loss of zinc during the process is very large; we obtained only 200 grammes from the original 760 grammes. Of this zinc 170 grammes were tested in Otto's apparatus with pure acid, and in twenty minutes there began to form in the reduction-tube a brownish deposit, which, at the end of three quarters of an hour, was a sufficient evidence of the presence of arsenic. The deposit was as large as that obtained from the same Silesian zinc, before it had undergone this process of fusion with nitre. It has been already stated, under the appropriate head, that this process did not disembarass the zinc of the sulphur which it contained, and

\* Dinger's Polyt. Jour., 1842, LXXXIII. 205; from Jour. de Pharmacie, 1841, p. 625.

† Annales d'Hygiène Publique, 1839, XXII. 427.

there seems to be little reason for expecting the complete removal of the arsenic, inasmuch as the fused saltpetre can only be brought in contact with the external surface of the zinc, however finely the metal may be granulated. It is not inconceivable that a trace of arsenic in a zinc should be eliminated by Meillet's process, and that a sample, originally almost absolutely free from arsenic, should be so improved as to afford no perceptible mirror; thus Stein \* could not detect arsenic in a sample of zinc purified by this method, but as a general rule it will not be safe to rely upon this process for the conversion of arsenical commercial zinc into zinc fit for use in Otto's apparatus.

On this subject of arsenic in commercial zinc two opposite errors demand notice. On the one hand, not a few chemists have maintained that commercial zinc almost invariably contains arsenic, and that Marsh's test is untrustworthy on this account. Thus Persoz † states that the greater part of the zinc sold in Strasbourg contains arsenic, and in a previous paper, ‡ condemning Marsh's process, he remarks with truth, that even distilled zinc may give spots of arsenic. The opinion that all zinc contains arsenic, finds support in the quantitative determinations by Schaeffele of the amount of arsenic in French zinc, Silesian zinc, and Vieille Montagne zinc respectively. These determinations have been quoted in almost all the modern text-books, and have had in our opinion much more weight than they are really entitled to. Schaeffele determined the arsenic in his samples of zinc by two methods. The first was that of Villain, and consisted in counting the number of arsenic spots obtained from a given weight of zinc, and estimating the corresponding amount of arsenic by means of the following absurd rule:—one milligramme of arsenious acid will give two hundred and twenty-six arsenical spots two millimetres in diameter. The utter unfitness of this process for exact experiments is too obvious to need any illustration. In applying this singular method, Schaeffele completely dissolved one kilogramme of zinc in dilute *sulphuric acid*, but in this connection says not a word about the purity of the acid, of which he must have used at least one kilogramme and a half. The second method used by Schaeffele was essentially that described by Jacquelin, and consisted in passing all the hydrogen generated by a given weight (from 320 to 800 grammes) of zinc through a solution of chloride of gold; this solution was partially decomposed by the arseniuretted [sulphuretted ?] hydrogen, and when the zinc had been completely dissolved, the chloride of gold solution, which was supposed to contain all the arsenic of the zinc in the condition of arsenious acid, was further decomposed as completely as possible by means of *sulphurous acid*, and the precipitated gold separated by filtration. In the filtrate there

\* Jour. f. pr. Chem., 1851, LIII. 40.

† Ann. de Ch. et Phys., [3.] 1844, X. 507, note.

‡ Ibid., [2.] 1840, LXXIV. 432.

still remained a small amount of chloride of gold, which had escaped reduction by the sulphurous acid, and to separate this chloride from the solution of arsenious acid, distillation was resorted to. The retort in which the residue from the distillation remained was washed out with water acidulated with *chlorhydric acid*, and the liquid so obtained was added to the original distillate, through which sulphuretted hydrogen was then passed. The precipitated sulphide was collected on a filter, dried, and redissolved in *ammonia*; this ammoniacal solution was then evaporated to dryness, and the residue weighed as sulphide of arsenic. As the result of this complicated process, which involves the use of so many different reagents and vessels, Schaeffele obtained a quantity of arsenic which varied between two thousandths of one per cent of the weight of the original zinc, in that sample which contained the most arsenic, and two five-thousandths of one per cent in that which contained the least. The weight of the sulphide of arsenic, which was the final result of the analysis, in no case exceeded ten milligrammes. There is no certainty that this very small amount of arsenic was not derived from the acids used in the process, for Schaeffele merely states that his sulphuric acid, of which he used a very large quantity, was "absolutely free from arsenic," and the other reagents are said to be pure. The methods by which he insured this absolute purity are not even hinted at, and we therefore have no opportunity of judging for ourselves of the sufficiency of the processes employed to eliminate the arsenic from these reagents, of which two at least almost invariably contain appreciable amounts of that impurity. Quantitative determinations, in which the original weights are kilogrammes, and the final weights milligrammes, are trustworthy only when the processes are short and simple, and the reagents employed are proved to be above suspicion. The process of M. Schaeffele was long and complex, and his reagents, so far from being proved to be above suspicion, were in all probability the source of the arsenic which he attributed to the zinc. In the valuable paper which we have before cited, Karsten distinctly states that the Silesian zinc is free from arsenic, basing this statement upon experiments which in their general method closely resembled those of Schaeffele; he endeavored to decompose a solution of nitrate of silver by a stream of hydrogen generated by the zinc under examination, but though his process was analogous to that of Schaeffele, he was led to the diametrically opposite conclusion. Again, Schaeffele's second method was essentially the process which has been thoroughly studied by Jacquelin, who claims for it a delicacy\* equal to that of Marsh's process; and yet in Jacquelin's own hands this method detected no arsenic in the specimen of zinc which he examined.† We cannot avoid the conclusion, that the determina-

\* Ann. de Ch. et Phys., [3.] IX. 490.

† Ibid., 1843, [3.] VII. 189.

tions given in M. Schaeffele's thesis have no general significance, and have gained more credit than they deserve. Our observations conclusively prove that there are zincs in commerce which are not contaminated with arsenic, and it should be noticed that, while one of our pure samples (the Pennsylvanian) was of a zinc which is not yet manufactured in large quantities, the other was a specimen of the Belgian zinc, one of the most common and abundant of the commercial spelters.

We turn now to the discussion of the opposite error, namely, that arsenic is very rarely to be found in the zinc of commerce. On this point we need only quote the strong statements of the highest authorities. Regnault, in the Report\* to the French Academy on Marsh's process and its modifications, wrote: "It is easy to procure in commerce zinc and sulphuric acid which give no arsenic in Marsh's apparatus." With the proper understanding of what is here meant by "Marsh's apparatus," this statement is as true now as it was twenty years ago. The committee relied chiefly upon the production of arsenical spots on porcelain, and though they recommended a form of apparatus adapted for heating the arseniuretted hydrogen to redness, yet in this apparatus the reduction-tube was not drawn down to a fine bore beyond the heated portion of the tube, and the committee in their own experiments seem to have preferred the arsenical spots as affording the best evidence of the presence of arsenic. They completely dissolved 500 grammes of commercial zinc in dilute sulphuric acid, and obtained from the hydrogen evolved no sensible arsenical spot; the black residue they did not examine. The test to which we have submitted our acids and zincs is more delicate than that applied by the committee of the French Academy; Otto's apparatus is more sensitive than that used by this committee, and will detect the presence of arsenic in quantities too small to produce sensible spots. It is self-evident that the continuous deposition of arsenic from a stream of hydrogen as it flows steadily through a very fine tube for an hour or more, would exhibit an amount of arsenic too minute to give the slightest perceptible spot in the instant during which the porcelain surface is held in the burning jet of gas. The first reaction is prolonged and accumulative, the second is intermittent and instantaneous. Blancard,† in commenting upon the statement regarding the ease of obtaining pure zinc, which is above quoted from the Report, has remarked with truth, that many zincs of commerce, which give no *spots* by Marsh's apparatus, nevertheless contain sometimes antimony, sometimes arsenic, sometimes both.

The same explanation should accompany the statements of Orfila, with regard to arsenic in commercial zinc and acids. This distinguished toxicologist, in a very valuable paper on "The Means of being assured of the Presence of Arsenic," after remark-

\* Comptes Rendus, 1841, XII. 1076, and Ann. de Ch. et de Phys., [3.] II. 159.

† Dingler's Polyt. Jour., 1841, LXXXII. 425, from Jour. de Pharmacie, Sept. 1841, p. 543.

ing\* that the sulphuric acid and the zinc of commerce sometimes contain arsenic, nevertheless implies† that he has never obtained decided arsenical spots on porcelain from a commercial sulphuric acid, and subsequently makes this explicit declaration: "I declare that I have made this experiment (the test for arsenic by the production of arsenical spots) more than five hundred times with the sulphuric acid and zinc of commerce, bought of various manufacturers of chemical products, and have only found arsenic *three times*."‡ Our own experiments confirm the truth of this statement; of all the specimens of zinc which we have examined, not more than two contained enough arsenic to give spots on porcelain, and not a single sample of our sulphuric acid would have afforded that reaction for arsenic. So long as the chemist, employed upon a poisoning case, sought for arsenical spots alone, the little arsenic which his zinc might have contained could do no harm; it is only when important conclusions are to be drawn from more refined experiments, with a more delicate apparatus, that the arsenic so often present in zinc and acids becomes a matter of very serious concern. Our experiments prove that arsenic is contained, not in all samples of commercial zinc, but in a large majority of them; and it will be perceived that we arrive at this result without impugning in the slightest the accuracy of the experiments upon which the very distinguished chemists whose words we have above quoted based opposite conclusions.

*General Remarks.*—In all commercial zincs metallic lead is the principal impurity, and the only one which deserves quantitative determination, if we exclude those exceptional cases in which the zinc is only an incidental product, or in which a very bad ore yields a zinc contaminated by some special impurity. Such exceptional zincs have only a local interest, for they are produced in very small quantities. The zincs which find their way into commerce in large quantities are the Silesian and the Belgian, the French, English, and American being used at home.

*Silesian Zinc.*—The greater part of the zinc sold under this name is made from carbonate and silicate of zinc, and from these ores zinc of great purity can be obtained; but wherever blendeiferous ores are worked, or zinc-oxide, obtained as an incidental product in some other process, is mixed with the ores used, the resulting zinc may be expected to contain arsenic. The zincs which we may call collectively German, have been more thoroughly studied than any other of the zincs of commerce, and this must be our excuse for having examined so few samples of these spelters. It had been established by the analyses of Karsten, Wackenroder, Kerl, and others, that lead was their chief impurity, and that cadmium often occurred in them in noticeable quantities. We have demonstrated the presence of minute quantities of sulphur and arsenic in

\* Annales d'Hygiène Publique, 1839, XXII. 404.

† Ibid., 411.

‡ Ibid., 424.

those samples which we have examined, of the spelters which are produced in the largest quantity from the best ores. An extended examination of the zincs produced on a small scale at different works throughout Germany, would in all probability detect the same impurities; \* but the labor of the investigation would be out of all proportion to the interest and importance of the facts to be observed.

*Belgian Zinc.* — There is a very noticeable difference in the purity of different samples of Belgian zinc. The ore is a mixture of carbonate and silicate of zinc, and yields with care an excellent spelter, which contains but a small amount of lead and no arsenic. We have found other samples of the zinc that were not free from arsenic, which they probably derived from the blende and its associated minerals, which occur with the silicate and carbonate of zinc constituting the great bulk of the ore. Careful selection of the ore is evidently necessary for the purity of the resulting metal.

*English Zinc.* — Much of the English zinc is made from blende, and is therefore more impure than the zinc of other countries made from better ore. Our analyses show that the English zincs, on the average, contain more lead than any spelter except the Silesian, and we also found much more arsenic in them than in any other zinc, except perhaps the New Jersey. One specimen of English zinc yielded a clear but slightly colored solution in dilute sulphuric acid, and our subsequent analysis gave no explanation of this color; its general appearance suggested the possible presence of some organic matter in the solution, and we mention the circumstance, because it is the only clew which we have been able to find to Miller's remark previously quoted, namely, that zinc contains a peculiar carbonaceous matter.

*American Zinc.* — The New Jersey zinc is made from the red oxide of zinc, mixed with Franklinite, and from the published analyses of these minerals the natural inference would be that they should yield a zinc of excellent quality. Accordingly, we found that our sample of this spelter contained less lead than any except the Pennsylvanian zinc; but on carrying further the analysis of the zinc, we were surprised to detect the presence of copper in a quantity sufficient to admit of quantitative determination. The analyses of the ore afford no clew to the source of this copper, and we are unwilling to believe that it is a natural and necessary admixture in zinc prepared from this ore. The amount of arsenic contained in this spelter was unusually large, but is fairly derived from the ore, in which we detected distinct traces of arsenic. This zinc was also contaminated with sulphur, carbon, and tin, and on the whole was one of the most impure spelters which we examined.

\* For example, it would be difficult to imagine how a zinc free from arsenic could be made from the oxide collected on the "Zinkstuhl" in the process formerly used in the Hartz, or from the arsenical blende now worked at Freiberg (Saxony).

The purest of all the zincs which we have analyzed is that manufactured at the Pennsylvania and Lehigh Zinc Works, Bethlehem, Pennsylvania. This spelter dissolves in dilute sulphuric acid without leaving any appreciable residue, and therefore contains no lead; indeed, a trace of cadmium is the only impurity whose presence in the zinc we could confidently assert. The ore from which this spelter is made is the hydrated silicate of zinc (electric calamine), and it is not surprising that this mineral should yield zinc of singular purity, if the ore be carefully selected. We have stated above that our first sample of this zinc was free from arsenic, but that the second sample was not pure in this respect. At these works the oxide of zinc is manufactured, as well as the metal, and we learn from a letter addressed to Professor Brush by Mr. Wharton, the director of the works, that the crust from the oxide furnaces has now and then been worked into spelter, and that the ore used in making the oxide is less carefully selected than that which goes to the spelter-furnaces, and is much more likely than the latter to contain both blende and pyrites. This fact may account for the occurrence of arsenic in some specimens of this spelter, while the greater part of it, manufactured from carefully selected silicate of zinc, is perfectly free from that impurity. There seems to be no reason why zinc of uniform purity should not be obtained from this excellent ore.

*Pure Zinc.*—We have already referred to the difficulty of obtaining a pure zinc by reducing it from the oxide on a small scale; nothing but the direst necessity could induce us again to attempt the operation, although it has been recommended by many high authorities. Nevertheless it is by no means difficult to prepare a pure oxide of zinc, and manufacturers of pure chemicals, working on a larger scale than it is practicable for the chemist to do, might undoubtedly prepare from this oxide at moderate cost a really pure zinc. There are some processes of chemical analysis in which the contamination of zinc with metallic lead is a matter of importance, because it affects the accuracy of the results; but in these cases the difficulty can generally be avoided by discarding zinc altogether, and resorting to other methods of analysis. But in order to use Marsh's process for the detection of arsenic, the chemist must procure zinc free from arsenic, and there is no escape from this necessity; redistillation will not disembarass zinc of its arsenic, and the process of reducing zinc from a pure oxide is very laborious and uncertain; how then can zinc free from arsenic be obtained? There is but one satisfactory answer to this question. Pure zinc might certainly be made from the oxide by the manufacturing chemist, but at present the zinc labelled "pure" by those who sell chemicals is not to be relied upon, and the chemist must therefore test samples procured from the dealer in metals, until he finds a specimen of the pure zinc which is manufactured on a large scale, and is to be obtained in commerce.

*Note on the Precipitation of Zinc from Acid Solutions by Sulphuretted Hydrogen.*—In the earlier steps of this investigation, we were somewhat embarrassed by the precipitation of sulphide of zinc, when sulphuretted hydrogen was passed for several hours through solutions of sulphate of zinc containing a considerable excess of sulphuric acid. In studying the best method of avoiding the difficulty, we made a series of experiments which seem to us to reconcile statements of previous observers which were apparently at variance, and to put the subject in a clearer light than that in which former observations had left it. From nine experiments with an aqueous solution of sulphate of zinc acidulated with sulphuric acid, and nine similar experiments with chloride of zinc and chlorhydric acid, Calvert\* inferred that “zinc, even in very acid liquors, was freely and sometimes completely precipitated from them by sulphuretted hydrogen,” and that “the old method for the separation of salts of zinc from those of copper must in future be rejected as completely inexact.” On the other hand, Grundmann† has deduced from four experiments with a solution of sulphate of zinc, acidulated with chlorhydric acid, a rule for the prevention of this precipitation of zinc by sulphuretted hydrogen, and he also maintains that the separation of copper or cadmium from zinc can be satisfactorily performed by repeating two or three times the precipitation of the copper or cadmium by sulphuretted hydrogen, and taking care to maintain in the solution a certain specified excess of acid. Grundmann used in each of his four experiments, 10 c. c. of a solution of sulphate of zinc (containing 0.2118 gram. of oxide of zinc in 10 c. c.), and 100 c. c. of water; to this mixture he added in the first experiment 1 c. c. of chlorhydric acid (Sp. Gr. = 1.1.); in the second, 2 c. c.; in the third, 3 c. c.; and in the fourth, 4 c. c. In the first experiment all the zinc was precipitated, but in the last none. The following tables contain a series of experiments, which we devised in order to prove what might be inferred from some of Calvert’s experiments; namely, that this precipitation of zinc by sulphuretted hydrogen was dependent, not so much upon the relation of the amount of free acid to the zinc-salt in the solution, as upon the degree of dilution of the solution, and that the mere addition of water might determine this precipitation in a solution which remained perfectly clear before such dilution. For convenience of comparison, we have used in the experiments of Table I. chlorhydric acid, and a solution of pure chloride of zinc of the same strength, and in the same quantities which were employed by Grundmann, but have substituted for the sulphate of zinc which he used chloride of zinc, in order to avoid bringing together in the same solution the sulphate of zinc and free chlorhydric acid,—a complication which seemed unnecessary and undesirable.

TABLE I.

	H Cl. Sp. Gr. = 1.1.	Zn Cl Solution; .2118 gram. Zn O in 10 c. c.	Water.	Remarks.
1	1 c. c.	10 c. c.	100 c. c.	{ No precipitate at the end of half an hour; after 15 hours an abundant but not complete precipitation.
2			200 c. c.	{ At the end of 15 hours all the zinc was precipitated.
3			500 c. c.	{ The precipitation began in two hours, and when next observed (at the end of 24 hours) was complete.
4	2 c. c.	10 c. c.	200 c. c.	{ No precipitate in 4 hours; in 24 hours there was a large but not complete precipitate.
5			500 c. c.	{ No precipitate in 1 hour; after 18 hours an abundant but not complete precipitation.
6			1000 c. c.	{ In 18 hours all the zinc was precipitated.
7	3 c. c.	10 c. c.	100 c. c.	{ H S was passed three times, and the last time during 18 consecutive hours; no precipitate.
8			200 c. c.	{ H S was passed twice; the last time during 12 consecutive hours; no precipitate.
9			500 c. c.	{ Began to precipitate in $\frac{3}{4}$ hour; in 18 hours there was a large but not complete precipitation.
10	4 c. c.	10 c. c.	500 c. c.	{ H S was passed three times, and the last time during 18 consecutive hours; no precipitate.
11			1000 c. c.	{ H S was passed twice, during 15 hours each time; no precipitate.
12			1500 c. c.	{ Began to precipitate in 1 hour, and gave a dense but incomplete precipitate.

\* Report of British Association for Adv. Sci., 1855, p. 51.

† Jour. f. pr. Ch., 1858, LXXIII. 242.



TABLE II.

	H Cl. Sp. Gr. = 1.1.	Zn Cl Solution ; 6.6272 gram. Zn O in 10 c. c.	Water.	Remarks.
1	3 c. c.	5 c. c.	0	{ H S was passed for several hours, and the solution saturated with the gas stood over night; a slight cloudiness, not amounting to a precipitate, appeared. Do. do. do.
2	5 c. c.	5 c. c.	0	
3	8 c. c.	5 c. c.	0	
4	3 c. c.	5 c. c.	25 c. c.	{ H S was passed steadily for 24 hours. Precipitate larger than before dilution, but still very slight. Do. do. do.
5	5 c. c.	5 c. c.	25 c. c.	
6	8 c. c.	5 c. c.	25 c. c.	
7	10 c. c.	5 c. c.	0	{ H S was passed steadily for 28 hours, producing a distinct cloudiness. H S produced in 6 hours a marked cloudiness, which at the end of 40 hours had somewhat increased.
8	15 c. c.	5 c. c.	0	
9	20 c. c.	5 c. c.	0	
10	25 c. c.	5 c. c.	0	{ H S was passed steadily for 28 hours, producing a distinct cloudiness. H S was passed 6 hours and over night; a perceptible but very small precipitate. Five experiments, of which the results were not distinguishable; H S was passed thoroughly, and in each case a very slight precipitate was produced.
11-15	30-50 c. c.	5 c. c.	0	
16	10 c. c.	40 c. c.	0	

The experiments of Table I. sufficiently prove that this precipitation is caused by too great dilution, and that an amount of free acid which prevents the precipitation of zinc from a concentrated solution becomes insufficient when the solution is very much diluted. The precipitates produced in dilute solutions are readily soluble in strong acid. This precipitation of zinc from acid solutions seemed a more serious difficulty to Calvert than it did to Grundmann, because Calvert's solutions were, on the average, very much more dilute than Grundmann's, both with regard to the acid and to the zinc-salt which they contained. Calvert's strongest solution contained only as much free acid as Grundmann's weakest, and hence in Calvert's experiments there was always a free precipitation of zinc which was often complete, while Grundmann soon found a limit beyond which the precipitation was too trivial to be noticeable.

The precipitates obtained in the experiments of Table II. were so minute, that they could not be certainly proved to be sulphide of zinc, and were utterly insignificant in comparison with the amount of zinc-salt contained in the very concentrated solutions. The gradual increase in the amount of free acid from the first experiment to the fifteenth, did not prevent the formation of this slight precipitate, and in the sixteenth experiment, the cloudiness produced was no greater than in the fifteenth. In a concentrated solution, therefore, a small amount of free acid will practically prevent the precipitation of the zinc. We have observed that in almost all cases, even when there is no actual precipitate, sulphide of zinc is deposited on any scratches on the sides of the beaker, and forms an adhering ring at the end of the tube which delivers the sulphuretted hydrogen. With regard to the value of the process of separating copper or cadmium from zinc by means of sulphuretted hydrogen, it seems perfectly possible to avoid such a dilution of the solution under treatment as would cause the precipitation of the zinc, without falling into the opposite and equally dangerous error of having too much free acid in the solution. Martin\* has shown that copper, and several other metals of the same group, are not completely precipitated by sulphuretted hydrogen in presence of a certain excess of concentrated acid. Between these two extremes, it is undoubtedly possible to find a safe mean, which may be rendered doubly sure by resorting to the tedious reprecipitation recommended by Grundmann and by Fresenius;† but in most cases other methods of analysis can be used with less trouble and greater accuracy.

\* Jour. f. pr. Ch., 1856, LXVII. 371.

† Anleitung zur Quantitativen Chem. Analyse, 4te Aufl., 1858, p. 423.